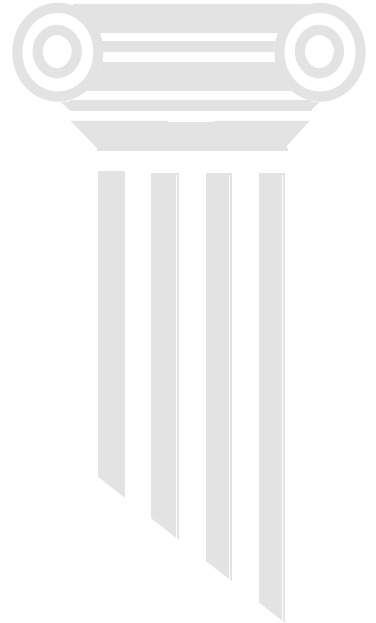
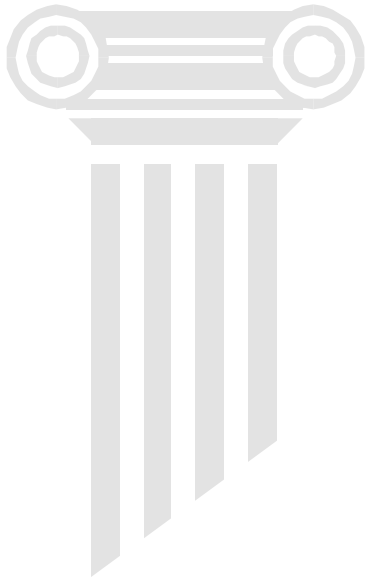


KINTECUS



“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, 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 the 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 at the same time 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.
- 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**.
- A very thorough 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**). Note that Kintecus will actually 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 fit the values against this interpolation. There is absolutely no need to “clean” your data, suggest interpolation methods nor specify timing meshes against your experimental data since Kintecus calculates values at exactly the times you specify in your experimental datafile. Kintecus V3.8 and above can also perform accurate **bootstrapping** of errors

- The ability to 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.
- Full output of **global normalized sensitivity coefficients** selectable at any specified time or times. Normalized sensitivity coefficients are used in accurate mechanism reduction, determining which reactions are the main sources and sinks (network analysis) and which also shows which reactions require accurate rate constants and which ones can have essentially guessed rate constants.
- The ability to 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 affects, 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.
- A powerful parser with an automatic mass & charge balance checker for those reactions that the graduate student "supposedly" entered in correctly but the model is yielding 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)9)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 is able to 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 smart mass balance can be used for biological and nuclear reactions! Kintecus also provides duplicate reaction and species checking.

- Built in support for special 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.
- As you can see in the above reaction, **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!
- Easily 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 through out 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.
- **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!** In fact, 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.
- 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.
- Perform complex hierarchical **cluster analysis** on temporal concentration profiles of the network with/without experimentally obtained temporal concentration profiles. Hierarchical cluster analysis in Kintecus has the ability to group related and unrelated parts of temporal concentration profiles in a meaningful, quantitative way. This grouping allows a user to clearly see patterns that were initially indiscernible or hidden.
- The ability to compute all internal **Jacobians analytically**. This is very useful for simulating very large kinetic mechanisms (more than 50,000+). Finite difference methods can cause underflow or overflow errors in approximately such 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

Running Kintecus in Command Mode

On the Windows Start button select RUN, type “command” (in **Windows-XP** type “**cmd**” instead of “command”, if you are 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 or cd “c:\program files\kintecus”, note the double-quotes). 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**”.

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 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 others.

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 one of the sample xls workbooks and edit the model, species or parm data worksheets. Afterwards, you can run/plot your model by clicking on one of the buttons located on the CONTROL worksheet.** If you are not going to use a spreadsheet, it's recommended to use a text editor (such as MS-DOS's "EDIT" or UNIX's vi or emacs) and use a comma 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 backward step having a [reverse rate constant](#), k_b , of one (1.0) if [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: | , the comma, TAB in the spreadsheet cell unless you are using a text editor in which case you 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 in 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 originally created the model.dat file with Excel, then the ADDSPEC.TXT file should load easily 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. As a note, whatever character was used to separate the fields in the model.dat file, Kintecus will use that same character for all its output files. This means that if you are using another spreadsheet program (like Lotus) and you save the model.dat spreadsheet as a text file for Kintecus to load, the ADDSPEC.TXT file will have commas in it too. For Excel, you should see something like this:

# Species	Residence	Initial	Display Output	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 containing the concentration profile of all the species that are being displayed are 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 time of the simulation, 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 make sure 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 a number of 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 of the settings in the parameter description spreadsheet usually do not have to be changed, but it is a good idea to know what exactly each field is.

****EXCEL FEATURE:** If you are utilizing the Excel graphical interface and have a Kintecus-Excel workbook loaded then 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 right after one clicks the "RUN" button located 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 is in Kelvins. If your model is not using the Arrhenius expression, special reactions or thermodynamics then this field is not used. You can also enter a filename here containing a temperature program. If you do wish to use a program

temperature then please skip to 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 accepts two values: “Yes” or any entry other than “Yes” (which translates to Kintecus, ignore this field). If you specify “Yes”, then the volume of the system will change to keep all gaseous products at the same exact pressure the simulation started. Kintecus calculates the starting pressure from summing all gaseous species’ concentrations, and then multiplying that by the gas constant, R, and temperature.

The **volume profile** fields allows one to enter a perturbation file (see the species spreadsheet file section for a full explanation on the types of perturbations allowed) containing the volume profile of the system through a simulation run. This allows 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) 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.

Note that if you running a simulation under constant pressure and you wish to have your energy input scale with the increasing or decreasing size of the volume (if volume increases by 2x, then the energy input decreases by 2x), add the “-cphs” (constant pressure heat source) switch to the Kintecus command line.

The **DAYS, Hours, Minutes, Seconds and PicoSecond** fields control the length of the simulation. This easily allows 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 $\exp(-E_a/RT)$). If you are not using the expanded Arrhenius equation then 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/cm³ 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. $M + hv \Rightarrow M + e^-$). 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 determine the total length of the hv profile. If the time of your run 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 an 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 slight distortion at 20% but can drastically reduced the size of the concentration file. This field is extremely useful for cutting the size of models that run for simulated years. A value of 7% is good for knowing how high certain peaks in concentrations you might be interested in. 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 very important.

Accuracy determines how far out in the decimal place to keep the concentration accurately computed. Therefore, a value of 1.0E-9 will keep the first nine digits of the integrated concentration accurately computed. 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 which can be specified on the command line. Please see the Kintecus switches section below on these extra options.

The **Starting Integration Time** (in seconds) determines the starting time step to integrate your model. After the first integration, this will change and grow larger if your accuracy is large and/or the stiffness of your model is low (meaning a decrease in execution -time of the program) , or grow smaller if your accuracy is very small and/or the stiffness of your model is high (meaning an increase in execution time of the program). You should not have to change this in most 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 troubling near the very beginning of the simulation run.

The **Maximum Integration Time** has a few uses in Kintecus. If you are not using a concentration profile on any species (see below in the [Species Description Spreadsheet](#)) and the '-obeymaxint' switch is given on the command line, then 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 fine for simulations lasting from 10 minutes to a few days respectively, but if you are doing simulation which only last a few nanoseconds, then a value of a few femtoseconds (1×10^{-15}) should suffice. If you only have, some species loaded as a concentration profile (see below in the [Species Description Spreadsheet](#)) then this will determine how often the data is retrieved from the concentration profile files. Reducing the maximum integration time will output more concentration values. If you have a final model and you wish to have a nice plot full of points that looks good for publication, you can try reducing this field by 10/100/1000 and so on. Don't forget to use the '-obeymaxint' switch to force Kintecus not to use time steps that exceed the value in the "Maximum Integration Time". Although, be warned, the simulation time 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 currently 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 allows one to specify the global temperature for all the inlets of a CSTR/PFR run. Depending on the flow (residence time in the Species Description Spreadsheet below), External Concentration (located also in the Species Description Spreadsheet below) and batch reactor/CSTR/PFR temperature and whether the pressure is constant or not, this will allow an additional cooling or heating affects.

Fields that have 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 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 right after one clicks the "RUN" button located on the CONTROL worksheet.

The fields in the Species Description Spreadsheet are:

#	Species Description Spreadsheet						
# Species	Residence	Initial	Display	External	Species Special	Constant File?	
#	Time in CSTR(s)	Conc.	Output (Y/N) ?	Conc.	Directives (/N)	(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 obvious in what they represent. 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. An important note is that 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 **very important** 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 then 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 special format. The format is that the very first line that contains 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 very last data point in the constant file, Kintecus will start over in the constant file using the very first data point and continue onward. If the very first line (the time spacing) has a minus sign in front of it, Kintecus will go through the entire data series once then automatically place the very last value in the datafile for the rest of the simulation time. Confused? Okay, here's some examples:

Examples:

In the Profile_A.TXT file contains these values:

```
43200
2
1
```

For a species that has the filename Profile_A.TXT in it's "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 where then the species concentration will drop to 1 Molar, at 86401 seconds the species will go back up to 2 Molar and this will repeat. Now, if the 43200 were -43200, then at time 86401 the concentration of the species will goto 1 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. Similar to the "-ADD" suffix described above where by the species is still a variable, but 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 also sound similar to the standard "Constant File" described above, but the species is still a variable, it is not constrained at the current SET value. Since the species is still a variable and not a constant, the species (or temperature or volume) will probably 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

There are many Kintecus kinetic and equilibrium examples using various types of perturbations described above. The "Gas Desorption off Tungsten" Excel file (its also the wolfrum.bat file) uses a temperature program file. The Kintecus-Excel models, "GRI MECH 3.0+Compression+Heat" utilizes both a temperature profile and a volume profile. Most of the equilibrium examples in the /EQUIL/ subdirectory use a Constant File for species concentrations (to construct phase diagrams) and/or holding the temperature of the system at a defined value. The Excel file, "H2_O2_Equil_Phases.xls" (its 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" (its 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 indeed very powerful techniques to study various perturbation methods to kinetic systems with the slightest of ease! Of course, you can have very long perturbation files (upto 25,000 points)! **The above descriptions on using perturbation files can also be used the same exact way 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**, that 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.

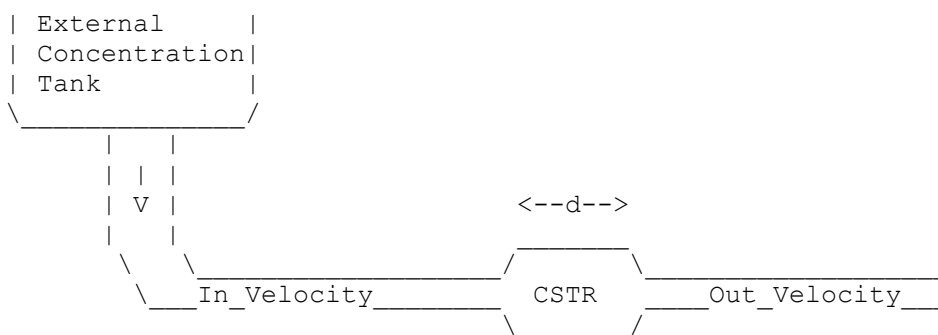
would become

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

Dr. Theodore Dibble (at www.esf.edu) has some nice spreadsheets to calculate some SZA's at various lat.-long. over time that you can "shove" 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) demonstrates this technique and although the animation shows a temperature program, the steps to make a "Constant File" are exactly 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. Actually, ANY worksheet prefixed with "O_FILENAME" will be outputted by Excel 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 for 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 that it will become once it is diluted in the CSTR before any reactions take place. A rough approximation of the residence time in a CSTR can be calculated as follows: $2 \times d$ (the distance across the CSTR parallel to the in/out flow) / (In_Velocity+Out_Velocity). You can have different residence times for different species.

If 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**, the SSA stands for Steady-State Approximation and it is not used in this version. You should never use SSA's. It has been shown repeatedly [2,3] that doing SSA's without knowing the actual output can result in disastrous results. In future versions of Kintecus, this field will change 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) and are currently utilized as a method 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 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 CH₃CH₂CH₃ or CH₃(CH₂CH₂O₂)₉₀₀₀₀CH₃ or Pu₂U₃Pr₄₃ or C₁₀₀₀₀₀H₂₀₀₀₀₂. 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 + 5H₂O ==> 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. This can be overridden 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 as 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** right after one clicks the "RUN" button located 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 are using the Excel graphical interface and have a Kintecus-Excel workbook loaded then the MODEL.DAT file as 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 right after one clicks the “RUN” button located on the CONTROL worksheet.

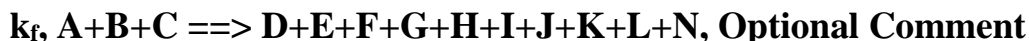
The fields in the Model Description Spreadsheet and some possible reactions listed are:

# Sample				
# Reactions				
#				Optional
# A	T ^m	E _a	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:



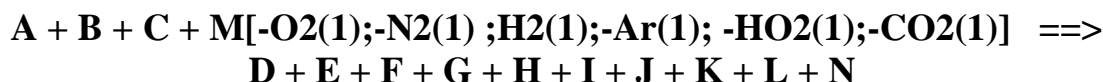
OR



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 as a means to enter the

reactions, then by default 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 three unique reactants and three 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 98H₂O or possibly 4.2343E-23H₂O. Signs can be postfixed to a species such as Cl⁻⁻⁻⁻⁻ or H₃O⁺ and even ylides and zwitterions such as C₈H₁₅P⁺⁻ (which will have no overall charge.). 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 very important 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.



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:



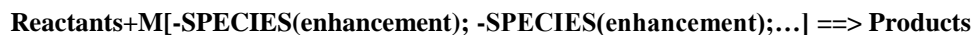
as shown in Sample Reaction 2. The difference between “regular” M (Sample Reaction 3) and M[..] is shown by the following two equations:

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

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

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 very important 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**. 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 through the prefixing the enhanced body by a dash, “-“. More than one species can become an exclusive third body (rate constants/parameters not shown below):



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 represented as follows:



OR



The A_0 , m_0 , E_{a0} are values used in the Arrhenius rate expression at the low pressure limit:

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

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:

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

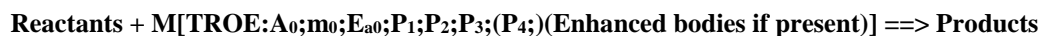
The F parameter shown above is always one for Lindemann reactions. Sample Reaction 8 in Figure 8 shows a Lindemann reaction with no enhanced third bodies. Sample Reaction 9 shows a Lindemann reaction with enhanced third bodies.

Troe Reactions

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



OR



The A_0 , m_0 , 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 Troe parameters P_1 , P_2 and P_3 (P_4 is optional) allow Kintecus to compute the Troe Factor, F :

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

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

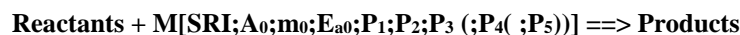
$$n = 0.75 - 1.27 \log F_{cent} \quad \text{Eqn 7.}$$

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

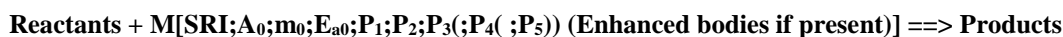
Once F is computed, it is inserted into equation 4. In some references **P₁=a, P₂=T***, P₃=T* and P₄=T****. Examples of the Troe reaction (with and without enhanced third bodies) in Kintecus are shown as Sample Reactions 5,6 and 7 in Figure 8.

SRI Reactions

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



- OR -



The A₀, m₀, 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 **P₁**, **P₂** and **P₃** (**P₄** is optional, and if **P₄** is supplied **P₅** is optional) allow Kintecus to compute the SRI Factor, F:

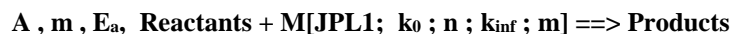
$$F = \left[P_1 \ell^{\left(\frac{-P_2}{T} \right)} + \ell^{\left(\frac{-T}{P_3} \right)} \right]^X P_4 T^{P_5} \quad \text{Eqn 9.}$$

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

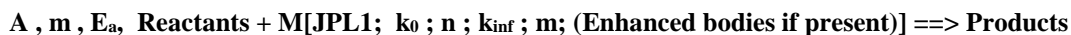
In some references **P₁=a, P₂=b, P₃=c, P₄=d and P₅=e**. Examples of the SRI reaction (with and without enhanced third bodies) in Kintecus are shown as Sample Reactions 10 and 11.

Jet Propulsion Kinetic Forms 1 and 2

Jet Propulsion Laboratory 4-parameter fit to the Troe expression (see section 2 at <http://jpldataeval.jpl.nasa.gov/download.html>) :



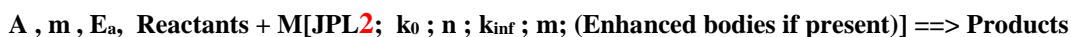
- OR -



and JPL form 2:



- OR -



Note that your concentrations *must* be in molecules/cm³ !! The A, m, and E_a values present before the reaction are utilized in the standard Arrhenius rate expression.

Where

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

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

There are two forms depending on your reaction: JPL1 and JPL2:

JPL1:

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

And JPL2:

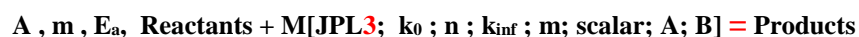
$$k_f^{ca}([M], T) = \left(\frac{k_0(T)}{1 + \frac{k_0(T)}{k_\infty(T)/[M]}} \right) 0.6 \left\{ 1 + \left(\log_{10} \left[\frac{k_0(T)}{k_\infty(T)/[M]} \right] \right)^2 \right\}^{-1}$$

Eqn 14.

Jet Propulsion Kinetic Forms 3 and 4

Jet Propulsion Laboratory 4-parameter fit to the Troe expression (see section 2 at <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):

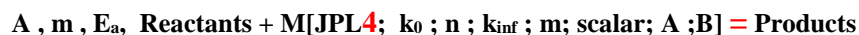


- OR -



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

and Jet Propulsion Kinetic Form 4 (JPL4):



- OR -



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:

$$k_r = \left[\frac{k_f([M], T) * \text{scalar}}{K_{eq}} \right]; \quad K_{eq} = A e^{\left(\frac{B}{T} \right)}$$

Eqn 15.

Again, it is important to note that you need to utilize the **the equal sign, “=” utilized 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 units for the rate constants are normally molecules/cm³, but supply any value for **scalar** other than one or zero can allow conversions to different units.

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 , Ea, 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. 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 be sure to 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**” and “**AramcoMech3.0_HAS_PLOG.xls**”.

Special Reactions

Special reactions are reactions that 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:



The parameters A, m, E_a, P₁ and P₂ are used to compute the forward rate constant:

$$k_f = AT^M \ell^{\left(\frac{-E_a}{RT} + \frac{P_1}{\sqrt[3]{T}} + \frac{P_2}{\sqrt[3]{T^2}} \right)} \quad \text{Eqn 16.}$$

In some references m=β, E_a=E, P₁=B and P₂=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:



- OR -



For TRANS1, the parameters A, m, b₁, b₂ to b_n and the optional c₁, c₂ to c_n are utilized to compute the forward rate constant in the following manner:

$$k = \frac{1}{\left(\frac{1}{AT^M \ell^{\left(\frac{-E_0}{RT} \right)}} + \frac{1}{b_1} + \frac{1}{b_2} + \left(\sum_3^{\text{upto10}} \frac{1}{b_n} + \left(\frac{1}{c_1} + \frac{1}{c_2} + \sum_3^{\text{upto10}} \frac{1}{c_n} \right) \right) \right)} \quad \text{Eqn 17.}$$

For TRANS2, the parameters A, m, b₁, b₂ to b_n and the optional c₁, c₂ to c_n are utilized to compute the forward rate constant in the following manner:

$$k = \frac{1}{\left(\frac{1}{AT^m \ell^{\left(-E_0/RT\right)}} + \frac{1}{b_1} + \frac{1}{b_2} + \left(\sum_{n=3}^{upto10} \frac{1}{b_n} + \left(\ln c_1 + \ln c_2 + \sum_{n=3}^{upto10} \ln c_n \right) \right) \right)} \quad \text{Eqn 18.}$$

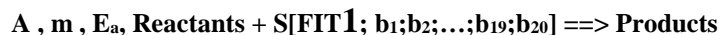
In some references b₁=kGa (kGa=Mass transfer coefficient of gas film) and b₂=De/R (De is the diffusion constant and R is the particle diameter) or b₂=La where La is the mass transfer coefficient of the liquid film) and b₃ onward and all c's are all ignored. These higher orders are allowed to give one extra fitting options if needed in the model. You usually don't have to set these. If you do not specify anything higher than b₂, then Kintecus assumes not to include those extra terms.

For an example of this type of reaction, please see the “H2-O2-combustion-gas-liquid-catalytic-surface-test.xls” sample Kintecus-Excel worksheet.

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:



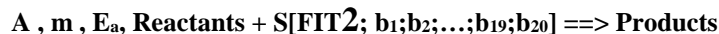
The parameters A, m, E_a, b₁ up to an optional b₂₀ coefficients are used to compute the forward rate constant according to this formula fit:

$$k_f = AT^m e^{\left(\frac{E_a}{T} + \sum_{n=1}^{upto20} b_n (\ln T)^n \right)} \quad \text{Eqn 19.}$$

The above FIT1 equation can be utilized with the reactions of 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:



The parameters A, m, E_a, b₁ up to an optional b₂₀ coefficients are used to compute the forward rate constant according to this formula fit:

$$k_f = AT^m e^{\left(\frac{E_a}{T} + \sum_{n=1}^{upto20} \frac{b_n}{T^n} \right)} \quad \text{Eqn 20.}$$

Chebyshev Fit

A , m , E_a, Reactants + S[FIT3;a;b; c₁;c₂;...;c₃₁;c₃₂] ==> Products

$$k_f = AT^m e^{\left(\frac{E_a}{T} \right)} \text{Chebyshev_polynomial}[a,b](c_1;c_2;...;c_{31};c_{32}) \quad \text{Eqn 21.}$$

Where [a,b] represents the temperature interval on which the original function func was evaluated with the Chebyshev Fit. The coefficients c₁, c₂, up to an option c₃₂ 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 is 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, c₁ upto c₃₂ will be outputted in the "chubcoefs.txt" file once you run the program. The numbers in the "chubcoefs.txt" file can then be directly entered right after the **FIT3** keyword. The program also outputs the original function along 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 make sure 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):

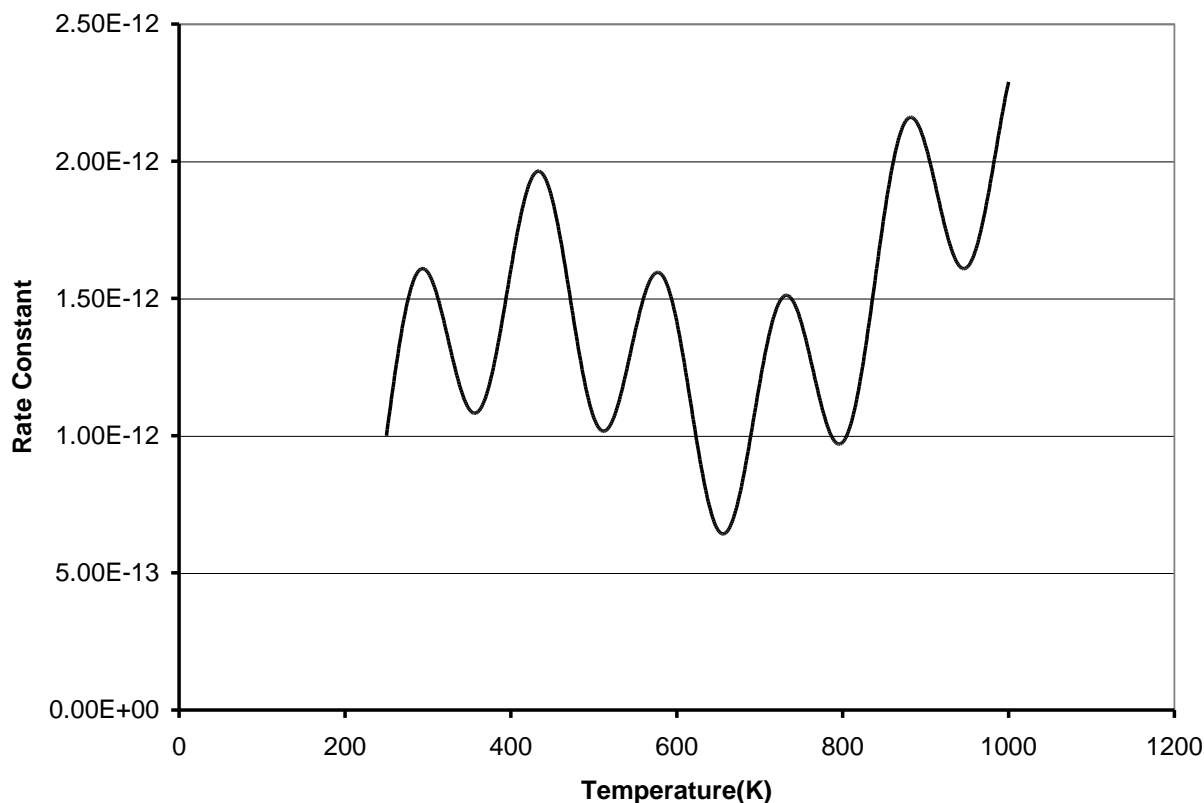


Figure 9. Sample Chebyshev Fit on a multi-sinewave. (see FORTRAN program below)

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 in 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 dependant rates of multiple well reactions. Please see those references for the list of equations that are utilized in Kintecus to calculate those rates.

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



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 contain 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:



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 is provided to allow users to convert the units from the rate to different units. It is usually set to one.

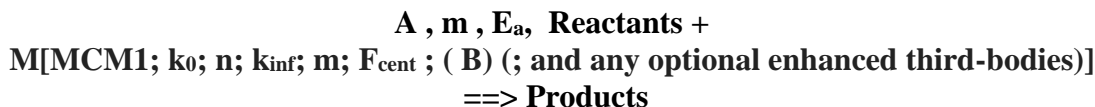
Master Chemical Mechanisms (MCM) Forms

Kintecus V5.5 and up now support some of the special IUPAC chemical kinetics forms from the Master Chemical Mechanism (MCM) (see <http://mcm.leeds.ac.uk/MCM/parameters/complex.htm> , <http://www.iupac-kinetic.ch.cam.ac.uk/> and/or http://iupac.pole-ether.fr/supp_info/Guide_2001.pdf or Google/Bing Master Chemical Mechanism). Most of these forms pertain with special pressure fall-off reactions that cannot be fully cast into the traditional Troe, Lindemann forms. Shown below are some 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 amount of parameters given. Also note that all rate forms shown below include $k(T)=A*T^m*\exp(-E_a/RT)$ 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 utilizes the Troe formalism and has several sub-forms depending on the amount of parameters given:



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

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.htm>). 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 bet set to 0.85 for KMT01).

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

➤ **MCM2**

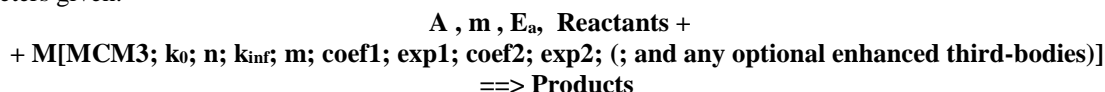
The MCM2 form utilizes the Lindemann like formalism :



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.htm>). 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**

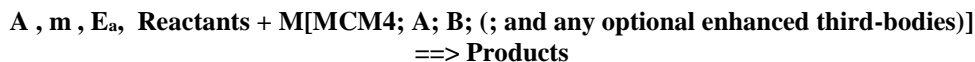
The MCM3 forms utilizes the Troe formalism and has several sub-forms depending on values of the last two parameters given:



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

➤ **MCM4**

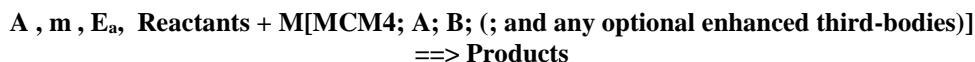
The MCM4 forms



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

➤ **MCM4 (no [M])**

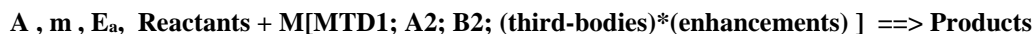
This “+S[MCM4]” form is exactly like “+M[MCM4]” but without the “[M]” term:



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

➤ **MTD1**

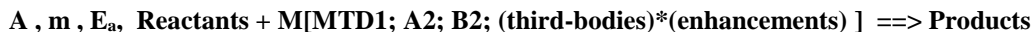
The MTD1 form is::



For the rate of $k(T) = A \cdot T^m \cdot \exp(-E_a/RT) \cdot (1.0 + (A_2 \cdot (\text{third-bodies}) \cdot (\text{enhancement}) \cdot \exp(B_2/T)))$. For example:
A, m, E_a, A+B+M[MTD1; A₂; B₂; H₂O(1.234)] \implies products will yield a rate of
of $k(T) = A \cdot T^m \cdot \exp(-E_a/RT) \cdot (1.0 + (A_2 \cdot [\text{H}_2\text{O}] \cdot 1.234 \cdot \exp(B_2/T)))$.

➤ **MTD2**

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



For the rate of $k(T) = A \cdot T^m \cdot \exp(-E_a/RT) \cdot (1.0 + (A_2 \cdot (\text{third-bodies}) \cdot (\text{enhancement}) \cdot \exp(B_2/T)))$. For example:
A, m, E_a, A+B+M[MTD1; A₂; B₂; H₂O(1.234)] \implies products will yield a rate of
of $k(T) = \text{[M]} \cdot A \cdot T^m \cdot \exp(-E_a/RT) \cdot (1.0 + (A_2 \cdot [\text{H}_2\text{O}] \cdot 1.234 \cdot \exp(B_2/T)))$.

➤ **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.htm>) and are shown below.

TDBR1:



Representing this form $A \cdot \exp(E_a/\text{TEMP}) \cdot (1 - 1/(1 + A \cdot \exp(-B/\text{TEMP})))$, so to represent :
 $3.8\text{D-}13 \cdot \exp(780/\text{TEMP}) \cdot (1 - 1/(1 + 498 \cdot \exp(-1160/\text{TEMP}))) : \text{CH}_3\text{O}_2 + \text{HO}_2 = \text{CH}_3\text{OOH}$, one would have
“ $3.8\text{e-}13, 0, 780, \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{S}[\text{TDBR1}; 498; -1160] ==> \text{CH}_3\text{OOH}$ ” in Kintecus notation.

TDBR2:

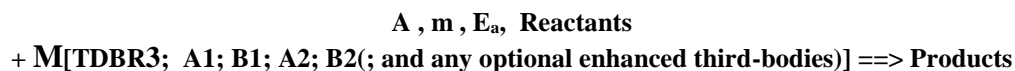


Representing this form $A \cdot \exp(E_a/\text{TEMP}) \cdot (1/(1 + A \cdot \exp(-B/\text{TEMP})))$, so to represent:
 $3.8\text{D-}13 \cdot \exp(780/\text{TEMP}) \cdot (1/(1 + 498 \cdot \exp(-1160/\text{TEMP}))) : \text{CH}_3\text{O}_2 + \text{HO}_2 = \text{CH}_3\text{OOH}$, one would have
“ $3.8\text{e-}13, 0, 780, \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{S}[\text{TDBR2}; 498; -1160] ==> \text{CH}_3\text{OOH}$ ” in Kintecus notation.

➤ TDBR3 to TDBR4

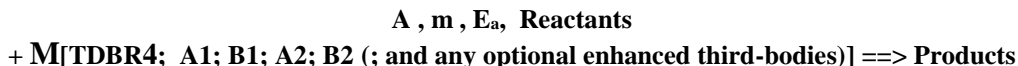
The Temperature Dependent Branching Ratio (TDBR) reactions forms also don't fit into one specific category, but they are listed in the MCM database (at <http://mcm.leeds.ac.uk/MCM/parameters/complex.htm>) and are shown below. Note the presence of “+M[“ and not “+S[“ as these reactions involve [M] unlike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

TDBR3:



TDBR3's form represents
 $A_1 \cdot \exp(-B_1/\text{TEMP}) \cdot (A_2 \cdot \exp(-B_2/\text{TEMP})) \cdot [\text{M}]$

TDBR4:



TDBR4's form represents
 $A_1 \cdot \exp(-B_1/\text{TEMP}) \cdot (1 - A_2 \cdot \exp(-B_2/\text{TEMP})) \cdot [\text{M}]$

➤ 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.htm>) and 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 = $k_1(T) + k_3[M]/(1 + k_3[M]/k_4)$ where $k_1 = 2.4 \times 10^{-14} \exp(460/T) \text{ cm}^3 / (\text{molecule} * \text{s})$;
 $k_3 = 6.5 \times 10^{-34} \exp(1335/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $k_4 = 2.7 \times 10^{-17} \exp(2199/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 = $9.5 \times 10^{-39} \exp(5270/T)/\{1 + 7.5 \times 10^{-29} \exp(5610/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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:

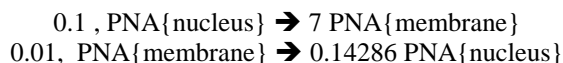
$2 * (K298CH3O2 * A1 * \exp(-B1/TEMP))^n$, where $K298CH3O2 = A2 * \exp(-B2/TEMP)$ the equivalent
 Kintecus SP4 syntax would be 2CH3C(O)O2+M[SPEC1; A1; B1; n; A2; B2;]==>2CH3C(O)OH

Kintecus will look for MODEL.DAT as the default filename. This can be overridden see KINTECUS Switches Section setting below.

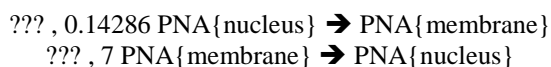
EQUILIBRIUM MODE NOTE: If you are running Kintecus in [equilibrium mode](#), then the Model Description Spreadsheet (model spreadsheet file) is NOT USED. Only the species description and the parameter spreadsheets are used for equilibrium runs.

Cell Compartments and Diffusion

You can use fractional rate-stoichiometric coefficients for cell compartments of different volumes. For example, to describe the peroxyxynitrate (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 (lets just say, $D=.1$, $D'=.01$) for PNA, the two reactions can be written as (keep in mind 0.14286 is about 1/7):



Now, 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.



It is easier specifying the change in volume through the products. An important side note, please stay away describing phases with one character, such as $\text{PNA}\{\text{a}\}$ or $\text{PNA}\{\text{g}\}$, as future versions of Kintecus will interpret the phases as real physical states and alter any related differential and/or algebraic equations. The current version of Kintecus only recognizes the gas phase, $\{\text{g}\}$, which can significantly alter gas-phase rates through $[\text{M}]$, 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 V6.01. You can use it to define your own chemical kinetic rate equations like this:

"A+B+S[USER;(variable list separated by commas) : (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"

(1) You must define all variables utilized in the function as a comma delimited list. You can use **T** for the current temperature, **P** for Pressure, **M** for Loseschmidt's value, **R** for gas constant, and **cXXXXXXX** for concentration of species XXXXXX, ie. concentration of CH4 would be **cCH4**.

(2) variables are limited to 10 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, atan, acos), hyperbolics (cosh, sinh, etc), square root (sqrt), absolute value (abs), exponent (exp) and other functions. For negative exponents (for example $1^{-0.6}$) you have to multiply it by minus one (-1), so $1^{-0.6}$ become $1^{(-1*0.6)}$.

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.

The Periodic Table SpreadSheet

This is another optional spreadsheet, which is 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 go into thermodynamic mode. Thermodynamic mode forces Kintecus to compute enthalpies, heat capacities and reverse rate constants (for any reversible reactions present) for all the reactions. To describe the temperature evolution of the system an ordinary differential equation (ODE) can be written as

$$\frac{dT}{dt} = - \left(\frac{1}{C_p(T)} \right) \sum_{i=1}^{N_s} \left(\frac{dc}{dt} \right)_i H_i(T) \quad \text{Eqn 22.}$$

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:

$$C_p(T) = \sum_{i=1}^{N_s} c_i C_{p,i} \quad \text{Eqn 23.}$$

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

$$\left. \begin{aligned} C_{p,i} &= R \left(la_{1,i} + la_{2,i}T + la_{3,i}T^2 + la_{4,i}T^3 + la_{5,i}T^4 \right) , \text{if } T_L \leq T < T_C \\ C_{p,i} &= R \left(ha_{1,i} + ha_{2,i}T + ha_{3,i}T^2 + ha_{4,i}T^3 + ha_{5,i}T^4 \right) , \text{if } T_C \leq T < T_H \end{aligned} \right\} \quad \text{Eqn 24.}$$

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

$$\left. \begin{aligned} H_i(T) &= RT \left(la_{1,i} + \frac{la_{2,i}}{2}T + \frac{la_{3,i}}{3}T^2 + \frac{la_{4,i}}{4}T^3 + \frac{la_{5,i}}{5}T^4 + \frac{la_{6,i}}{T} \right) , \text{if } T_L \leq T < T_C \\ H_i(T) &= RT \left(ha_{1,i} + \frac{ha_{2,i}}{2}T + \frac{ha_{3,i}}{3}T^2 + \frac{ha_{4,i}}{4}T^3 + \frac{ha_{5,i}}{5}T^4 + \frac{ha_{6,i}}{T} \right) , \text{if } T_C \leq T < T_H \end{aligned} \right\} \quad \text{Eqn 25.}$$

Equations 3 and 4 use the coefficients of la_{1-6} for the low temperature range, T_L to T_C , and the coefficients ha_{1-6} for the higher temperature range, T_C to T_H , are taken from the thermodynamic databases described in reference 5 above. As mentioned above, dc/dt is required in equation 1 and it also describes the time evolution of the concentrations of the species present in the system:

$$\left(\frac{dc}{dt}\right)_i = \sum_j^{products} k_j(T, P) n_{i,j} \prod_k^{reactants} A_k^{n_k} - \sum_j^{reactants} k_j(T, P) n_{i,j} \prod_k^{reactants} A_k^{n_k} \quad \text{Eqn 26.}$$

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,

$$k_r = \frac{k_j(P, T)}{\left(\frac{1}{RT}\right)^{\Delta n} \exp\left(-\frac{\Delta H(T)_r - T\Delta S(T)_r}{RT}\right)} \quad \text{Eqn 27.}$$

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

$$\Delta H(T)_r = \sum_{i=1}^{products} n_{r,i} H_i(T) - \sum_{i=1}^{reactants} n_{r,i} H_i(T) \quad \text{Eqn 28.}$$

$$\Delta S(T)_r = \sum_{i=1}^{products} n_{r,i} S_i(T) - \sum_{i=1}^{reactants} n_{r,i} S_i(T) \quad \text{Eqn 29.}$$

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

$$\left. \begin{aligned} S_i(T) &= R \left(la_{1,i} \ln(T) + la_{2,i} T + \frac{la_{3,i}}{2} T^2 + \frac{la_{4,i}}{3} T^3 + \frac{la_{5,i}}{4} T^4 + la_{7,i} \right) , \text{if } T_L \leq T < T_C \\ S_i(T) &= R \left(ha_{1,i} \ln(T) + ha_{2,i} T + \frac{ha_{3,i}}{2} T^2 + \frac{ha_{4,i}}{3} T^3 + \frac{ha_{5,i}}{4} T^4 + ha_{7,i} \right) , \text{if } T_C \leq T < T_H \end{aligned} \right\} \quad \text{Eqn 30.}$$

Again, the thermodynamic coefficients shown above are obtained from the thermodynamic database(s) which are 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 the course of a simulation to force those conditions.**

As noted above, 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 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://www.cms.llnl.gov/combustion/combustion2.html> .

If 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 then you will have to either perform experiments to obtain the heat capacities or compute the heat capacities. Methods to compute 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 show below:

# Database	Database		Species
# FileName	INPUT	MAP	Special Switches
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
freeoh1.dat	FREE	SP:LT:CT:HT:LA1:LA2:LA3:LA4:L	UPPL
#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 mean to provide multiple thermodynamic database 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 Species Reservation List explained below.

The INPUT and MAP columns 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 finally 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**. All keywords must be delimited by a **colon, “:”**. A full sample INPUT field is shown below:

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

The F() keywords directs Kintecus that here is an important field of length () characters. The IG() keyword directs Kintecus to “ignore” or skip () characters. The NL keyword directs Kintecus to go to the next line. The F() 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 in 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 show an example use of this feature.

The MAP fields converts 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 is a good indication 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 that 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 exactly 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 <u>and</u> 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 name 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 specifically 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 the need of deleting and re-inserting rows of data, which could lead, to a big mess. This allows one to test various thermodynamic values created by different authors or groups. As with all values in the thermodynamic description spreadsheet, the list in the Species Reservation List field must be delimited by a colon, “:”.

It appears 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 that 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 given 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/DARPA thermodynamic databases NEVER suffix a gaseous species name with (g), it is used only here as a demonstration. 2. It appears all NASA/DARPA 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 on the next page.

# Species #	LOW TEMP.	Common TEMP.	Hi TEMP.	Thermodynamic coeff. (LOW then HIGH)														
				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

Kintecus Command Line Switches

Kintecus provides a large number of 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:

```
-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 three: beginning, middle and the end)
    -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
 c=User Dataset Filename=Any allowed text filename
 If beginning of c="FITLINK", user defined equation constraints
 If c=fitdatan then perform global regression analysis
 If "c=fitdatan,filename" then perform global regression analysis with initial conditions
 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:X1:Y1[:X2:Y2:Xn:Yn] fit weights Y against fitdata column no. X.

-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" 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=Gaussian or 2=Uniform), 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 uncertainly runs. [KEEP]

-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]

Advanced Kintecus Switches:

-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 (-yle-40) .
 -cphs Alter heat source to scale with volume changes during constant
 pressure runs.
 -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/eigenvalues into jacobian000.txt
 files'
 -dynamic enable dynamic mode to control Kintecus in feedback
 -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 #.
 -obeymaxint Force Kintecus to obey the "Maximum Integration Time" field

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, the second number is the value to set that to the described parameter. The table below shows the number corresponding to the type of integrator parameter and the default value. Please keep in mind that integrators 1 and 2 should be sufficient for 99% of the chemical kinetics problems you might encounter. **Integrator #5 can also be utilized to 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%. It is **NOT** recommended to use the Gear integrator (-INT:3) with such constant-pressure simulations. 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) .

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 DVIDE 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) .**

Example, to change 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%, simply 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 utilized 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 various physical properties on the system which can help one's analysis.

Numerical Techniques

Sensitivity Analysis

Kintecus can generate normalized sensitivity coefficients at any time or times 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:

$$NSC = \left(\frac{\frac{\partial [Species]}{[Species]}}{\frac{\partial k}{k}} \right)_k = \left(\frac{\partial \ln [Species]}{\partial \ln k} \right)_k \quad \text{Eqn 31.}$$

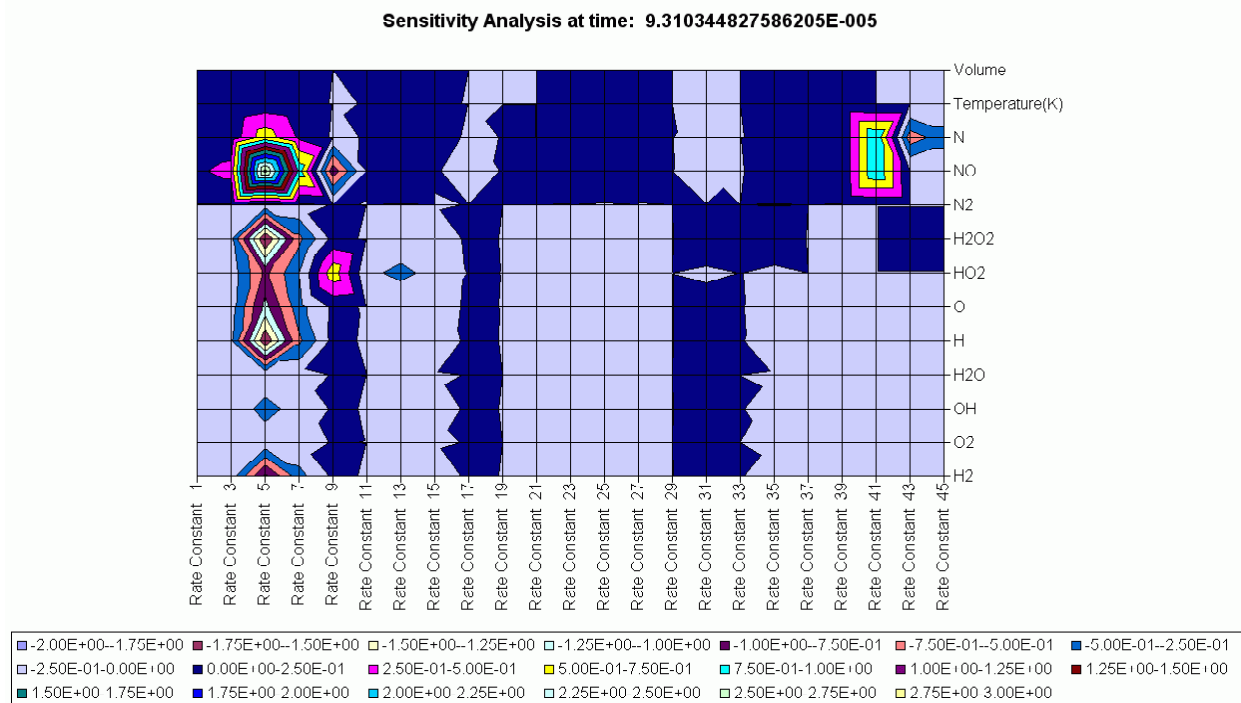
It is a matrix with signed numbers, which indicate the reactions that have the biggest influence on certain species. By examining the matrix and sorting the largest NSC's by reactions for each species one can see that the large positive NSC's are the major sources and the large negative NSC's are the major sinks[10]. A reaction that has a very small NSC for a species indicates that reaction has almost no influence on the species no matter what the rate constant or the reaction's concentration of reactant species. The method to make Kintecus actually 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 then 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 actually outputs the transpose of the NSC matrix (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 that, "Hey, if I just sum up the squares of the NSC's for each reaction then I'll know what reaction to drop because the reactions with very small NSC's should have no affect on any of the species". This might be true for most kinetic mechanisms, but in some cases this is not the case. NSC only tests for direct routes of influence of species X, it does not directly show strongly interacting reactions. A very simple method to see which

reactions can actually 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, **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, **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 correspond to reactions that have no overall affect 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 in an automatic manner and other advanced chemical mechanism analysis that is 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 one 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 newer 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 NSA plot is shown below taken from the "Combustion_H2_O2_sensit.xls" Excel workbook.



A new feature in Kintecus V3.96 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” $3 \times (\text{number of reactions}) \times (\text{\# of species} + \text{temperature} + \text{enthalpy})$ **partial derivatives** in temporal space to compute the last NSC matrix (SENSIT100.TXT for Case #1 and SENSIT005.TXT for the Case #2). Now it is possible that in Case #2 will finish ahead of Case #1 as Kintecus will try to take very large time steps, $(\text{total simulation time})/5$, to get the “marchers” to the end as quickly as possible. Case #1 is forced to take time steps no larger than $(\text{total simulation time})/100$ and so 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 time steps than Case #1. Large time steps can occasionally cause Kintecus to end up with extremely wild solutions causing Kintecus to “backtrack” or even crash. In Case #1 above, the time steps are smaller and so 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 is given. In fact, 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 size of very cheap hard disks today (250 GB for \$80.00) 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. If 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 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 Arrhenious expressions, thermodynamics, special/fall-off/[M] reactions or constant pressure settings.

Outputting Jacobians

Since the Jacobians are square matrices of the partial derivatives of $d(\text{Overall Species Formation-Destruction Equation}) / d(\text{Species/Temperature})$; it might be of use to some (those interested in finding Intrinsic Low Dimensional Manifolds or ILDMs) to have Kintecus output these Jacobians (and optional eigenvalues and/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" which will give filenames like JACOBIANnnn.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 Jacobian matrix (into separate file named jeigenvalues~~nnn~~.txt)

32=**output eigenvectors** of Jacobian matrix (into separate file named jeigenvectors~~nnn~~.txt)

Simply add up the numbers above into the -ojac switch for what you want. i.e. if you want 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), just 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, there is a new switch named '-obeymaxint' which will force Kintecus to obey the "Maximum Integration Time(s)" field in the parameter spreadsheet. This allows you to force Kintecus to take alot of steps and so to output alot of Jacobian files at very fine time intervals. Normally, "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.

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 11.

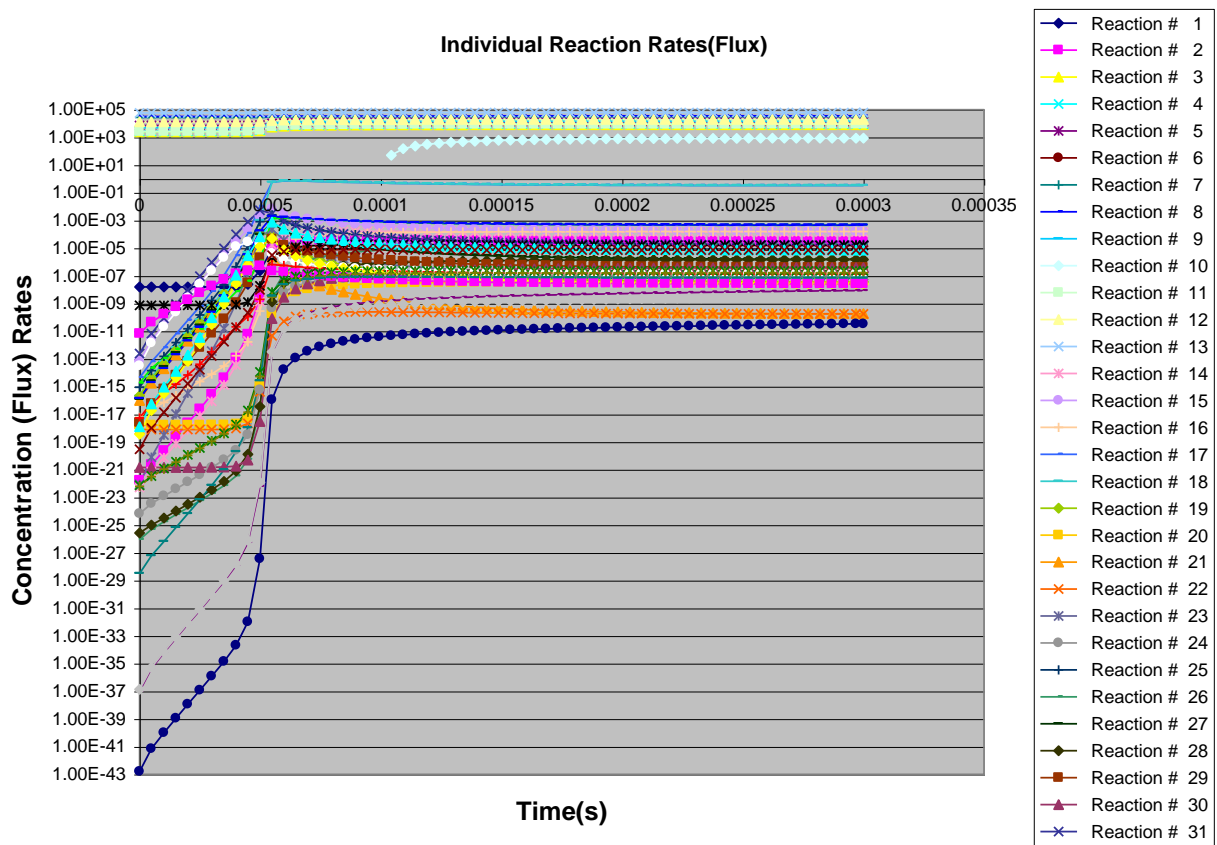
A new feature in Kintecus V2.3 is the ability to output various kinetic and thermodynamic results. By using the “-o” switch, these various system properties can be outputted in four separate files. The “-o” switch has four fields and **all four** must be included on the command line to output these properties: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

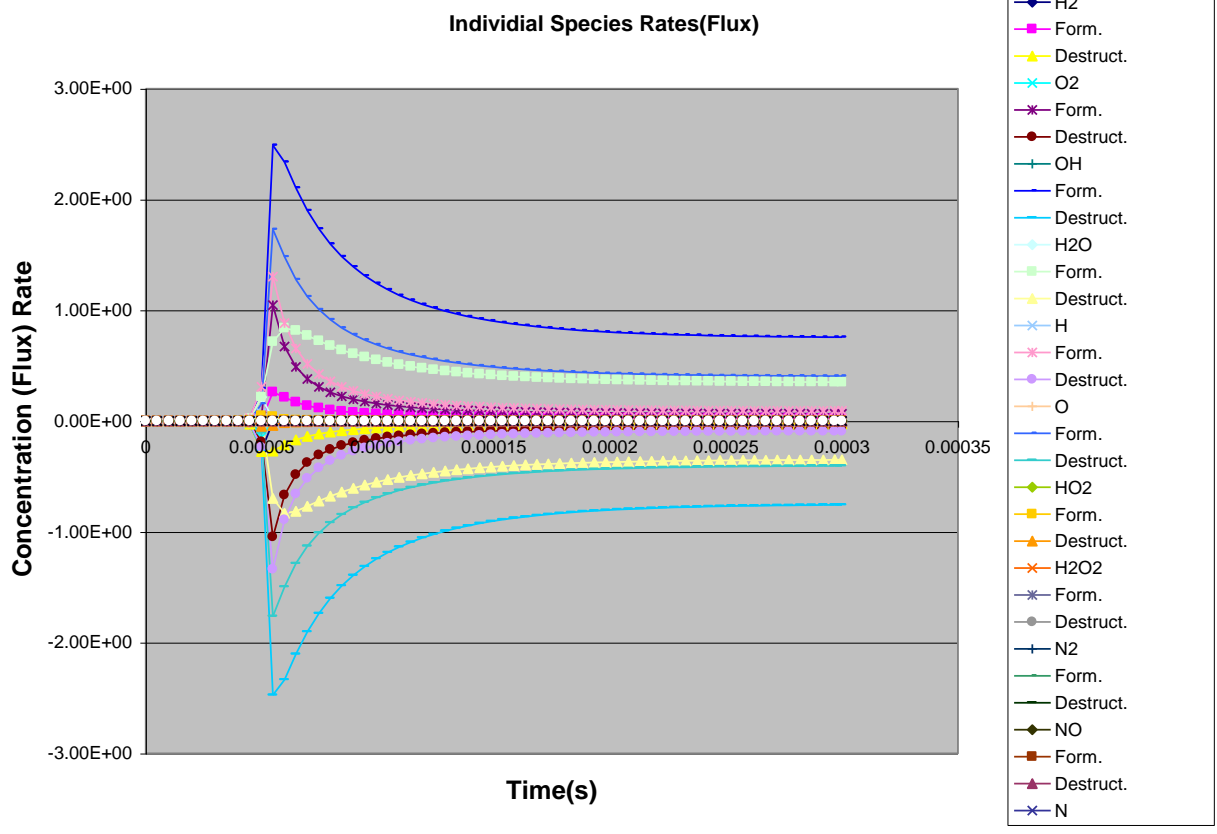
Field	Possible Values	File Created	What the File Contains
1	“Y” or “N”	RATESOUT.TXT	Each Reaction Rate: $d[\text{reaction}]/dt$ for each reaction ! (can be a lot of data)
2	“Y” or “N”	SPECRATE.TXT	Overall Species, Formation and Destruction Rates: $d[\text{species}]/dt$
3	“Y” or “N”	THERMOUT.TXT	Overall 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 amount 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 a lot of reactions and trying to output a RATESOUT.TXT or a SYSTEMOUT.TXT file. Conversely, to decrease the amount of points in any of the above files, you can increase the Maximum Integration Time in the Parameter Description Spreadsheet.

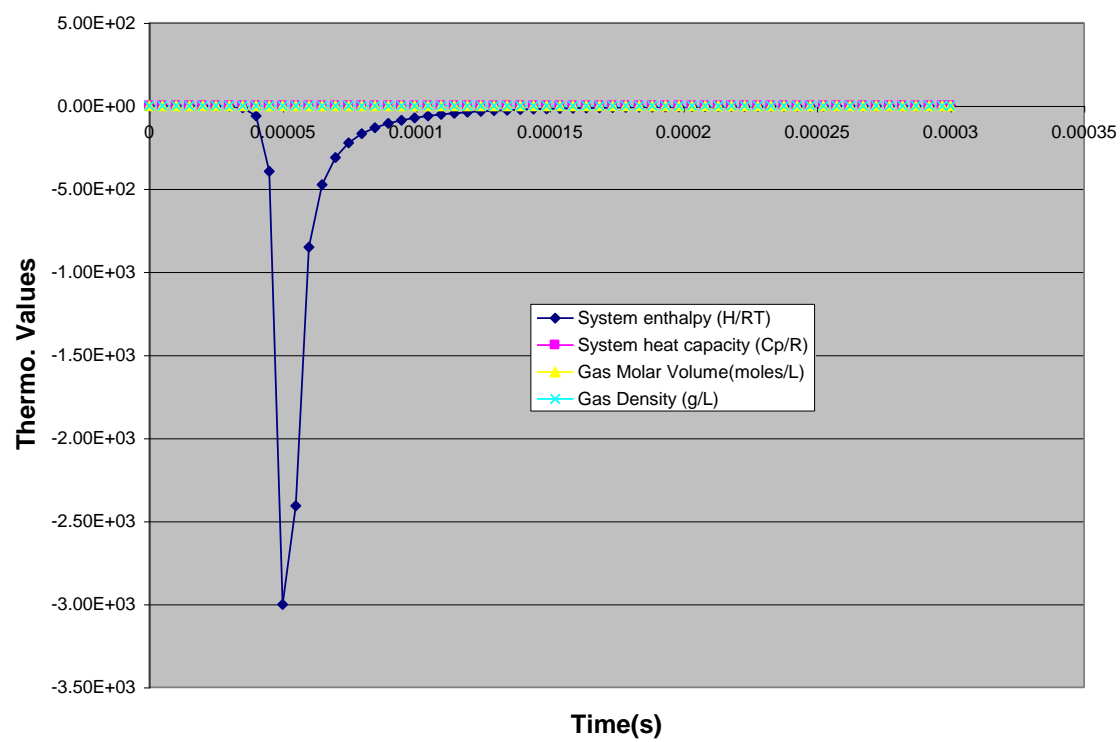
There are sample RATESOUT.TXT, SPECRATE.TXT, THERMOUT.TXT and SYSTEMOUT.TXT files created by specifying the additional Kintecus command line option -o:Y:Y:Y:Y for the adiabatic, constant pressure O₂ combustion model OH2.BAT .

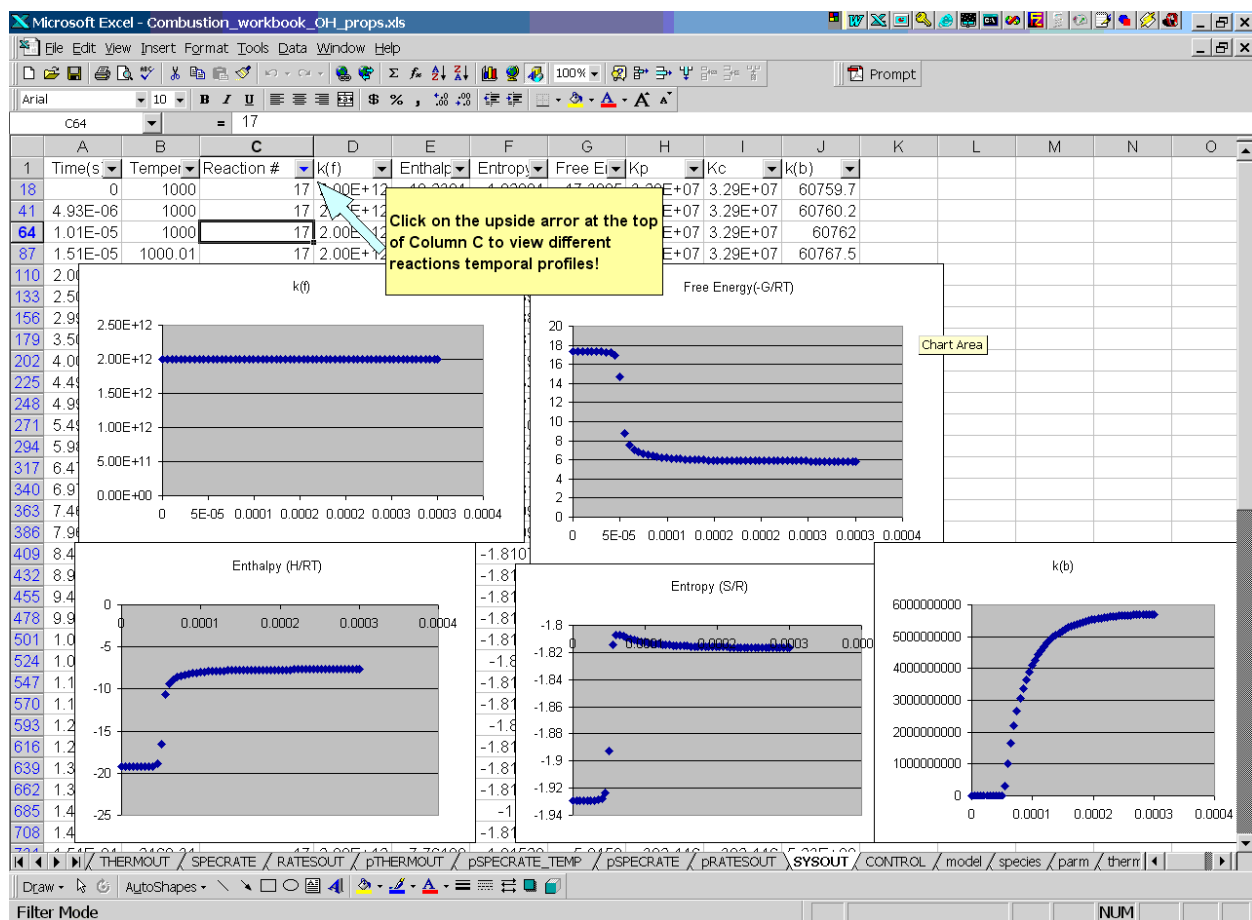
A new feature in the Kintecus V3.7 Excel worksheets and above is that the Excel macros will recognize the “-o” switch and automatically **look for and plot ALL FOUR output files!** The below four samples are from adding the “-o:y:y:y:y” switch to the “Combustion_OH.xls” Kintecus-Excel file command line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





System Thermodynamics/Energetics





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 2.9	Sinks 2.9	Terms 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, system properties, alter those properties, and continue. This allows one to control Kintecus dynamically in a feedback manner. Feedback control can be a very complicated and broad area which is beyond the scope of this document. Please consult an appropriate text book on this subject. Dynamic mode in Kintecus is invoked by including the

"-dynamic[:wait time]" switch on the command line. Currently there is only one method for interprocedure communication with Kintecus and it involves text files. A flow diagram in Figure 12 is shown on the order in which one can write an external program (in Excel VBA code, MATLAB, Python, etc.) to control Kintecus:

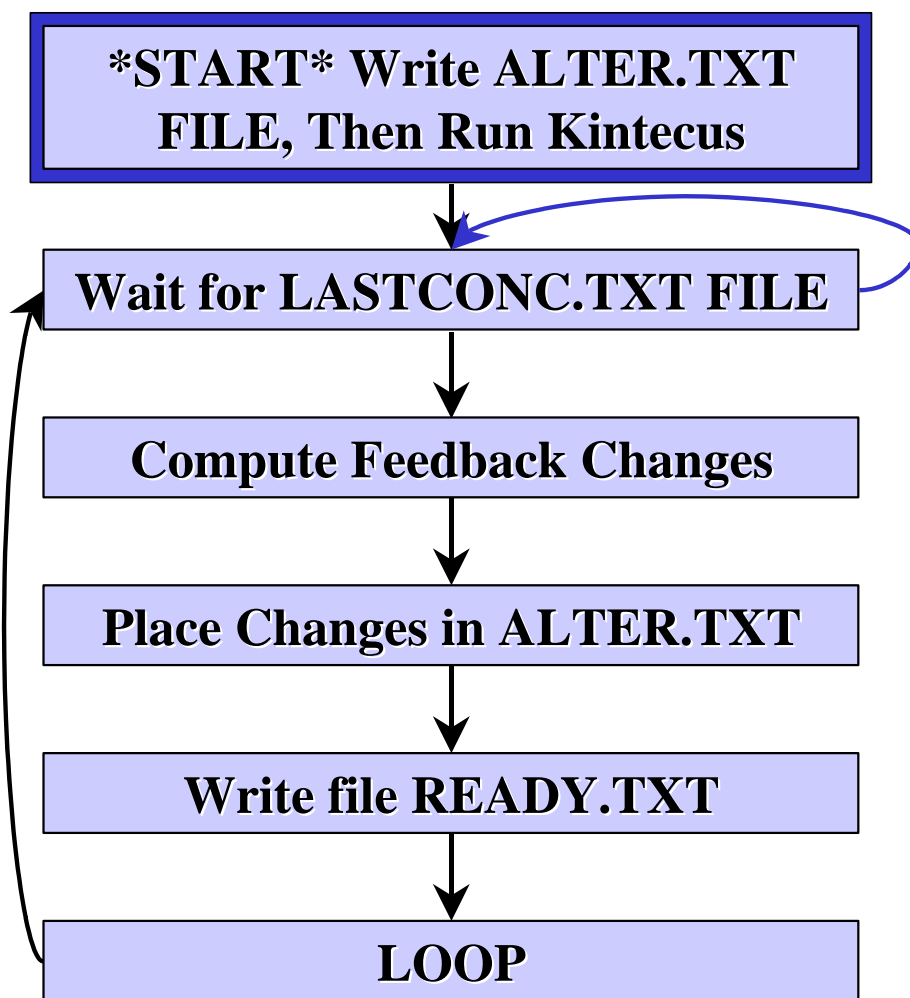


Figure 13. Asynchronous interprocedure communication flow control using three text files that Kintecus requires for dynamic mode. Socket asynchronous interprocedure communication not available in this version.

Three text files must be processed in order for a full feedback control of Kintecus. The first and only step executed once is shown in Figure 12, **"*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, 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 8 below for all possible values and Figure 14 below 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 place 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. The two columns are delimited by a comma, ",". The order of the species names and concentrations will not change during runs, BUT if a species is made into 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. During this waiting period, Kintecus is "pushed" into the background and consumes zero CPU cycles. The default waiting period is 200 milliseconds. One can change this waiting period by specifying the waiting time (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 very simple example is provided through using VBA scripts to control Kintecus in dynamic mode is provided as Excel Workbook, "[Combustion_H2_Dynamic.xls](#)". Most of the VBA code in the Excel spreadsheet demonstrating the Kintecus dynamic mode is simple overhead, the actual feedback loop is around line 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 ALTER.TXT file with automatic updates of two graphs provided in the "dynamic_plot" worksheet. Keep in mind, 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. The smaller version is provided if one wished to include Kintecus in a mass/fluid flow **1D/2D/3D-grid** calculations. However, because of the memory constraints, the Kintecus_small version can only handle about 800 reactions.

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 interactive mode:

File	When It Appears	What It Contains
KRUN.TMP	Kintecus starts up and is running. This file is deleted by Kintecus 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 on how to monitor these error exceptions. A new additional file is written in Kintecus V2.8. The name of the file is always view.txt and it will contain everything displayed on the screen plus some addition output redirected into this file. You must make sure no other application has the filename, "view.txt", opened in the same directory as Kintecus is running while using the interactive 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 alot of steps and so to output alot 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 amount of decimal places for the "Time(s)" column and concentrations/temperature columns that appear 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 and/or eigenvalues/eigenvectors of those Jacobians. The switch and its arguments are **-f:F:F**. Where the "F" stands for a FORTRAN Format Descriptor. The **default** FORTRAN Format Descriptor used is **"E14.6:E14.6"** . An example, if you need four more decimals places 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 can be used such as F, I or G, ie - **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.

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 simply 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. Here is the current listing of models completely transferred into Excel workbooks: [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](#).

The Smog Reaction Model

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

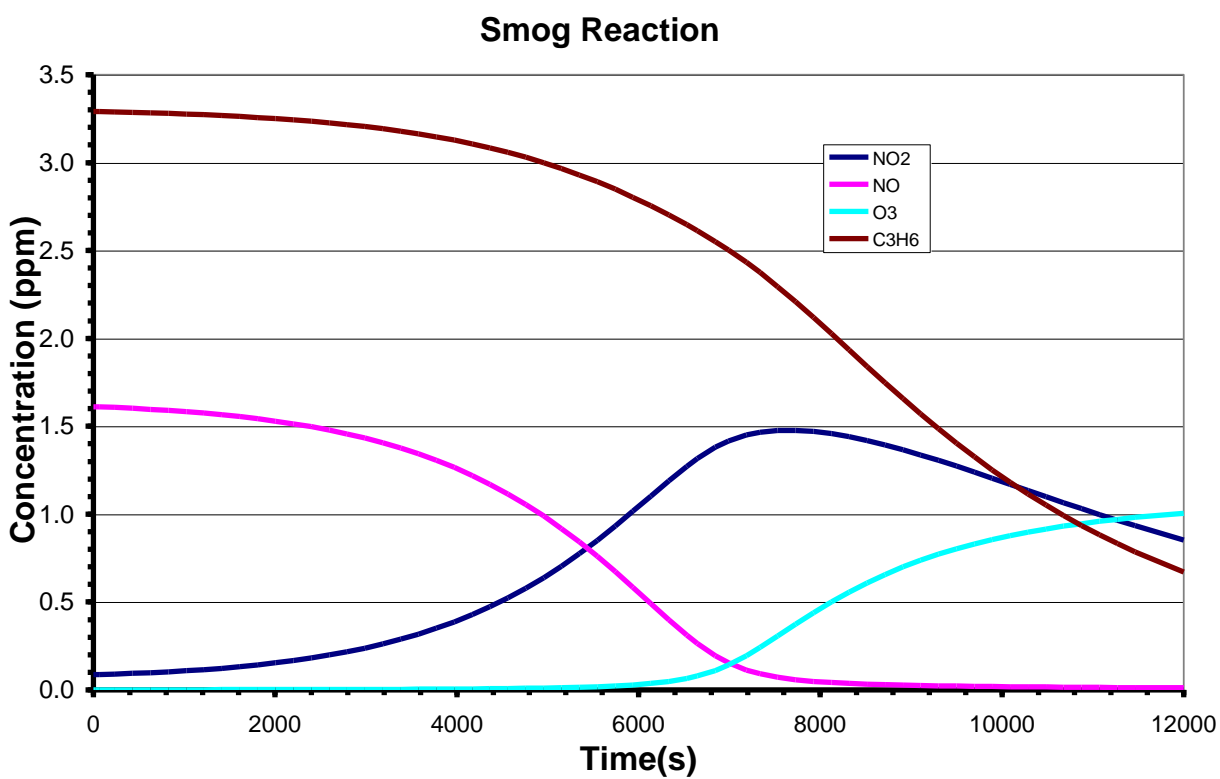
MODSMOG.TX2 - The kinetics reactions

SPECSMOG.TX2 - The species involved

PARMSMOG.TX2 - The parameters used

CONCSMOG.TXT - A simulation run.

SMOG.BAT - A very simple 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.

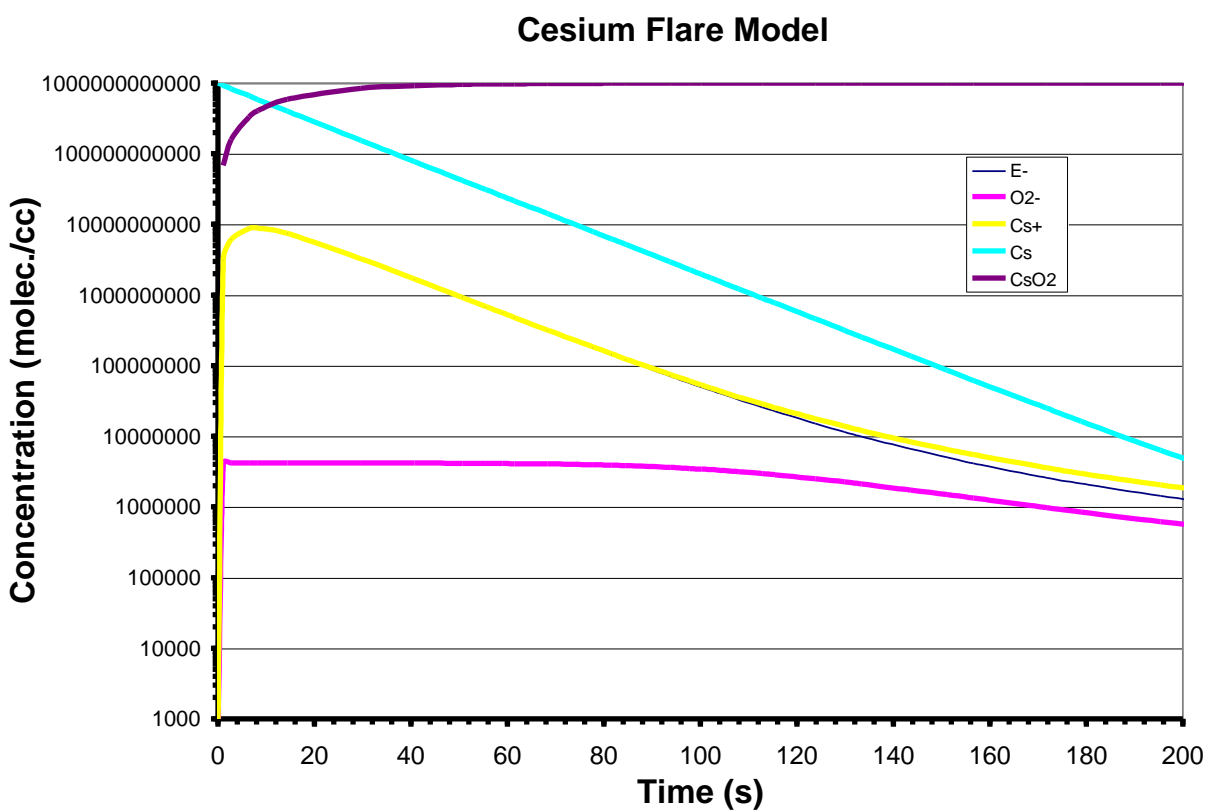
MODCES.TX2 - The kinetics reactions

SPECCES.TX2 - The species involved

PARMCES.TX2 - The parameters used

CONCCES.TXT - A simulation run.

CES.BAT - A very simple 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].

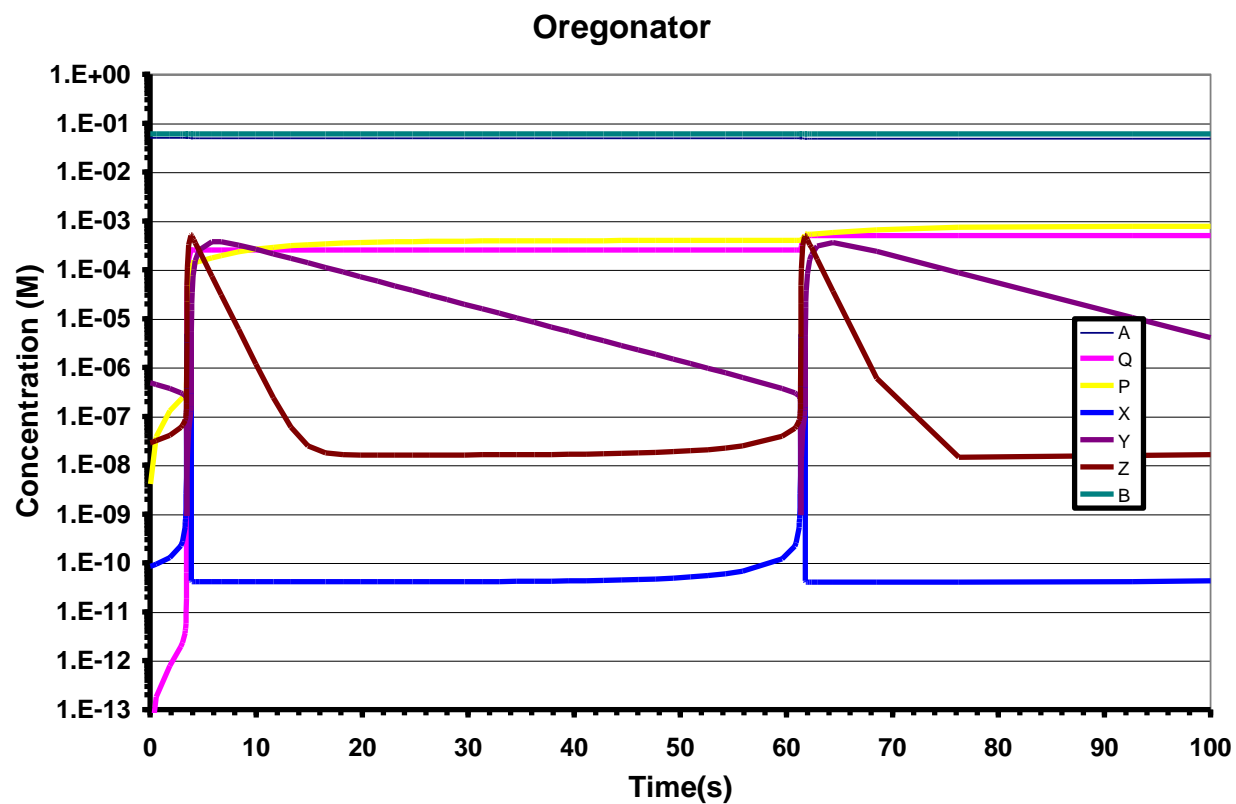
MODOREG.TX2 - The kinetics reactions

SPECOREG.TX2 - The species involved

PARMOREG.TX2 - The parameters used

CONCOREG.TXT - A simulation run.

OREG.BAT - A very simple 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, CONCASTIF.TXT, matches the results on page 89[6].

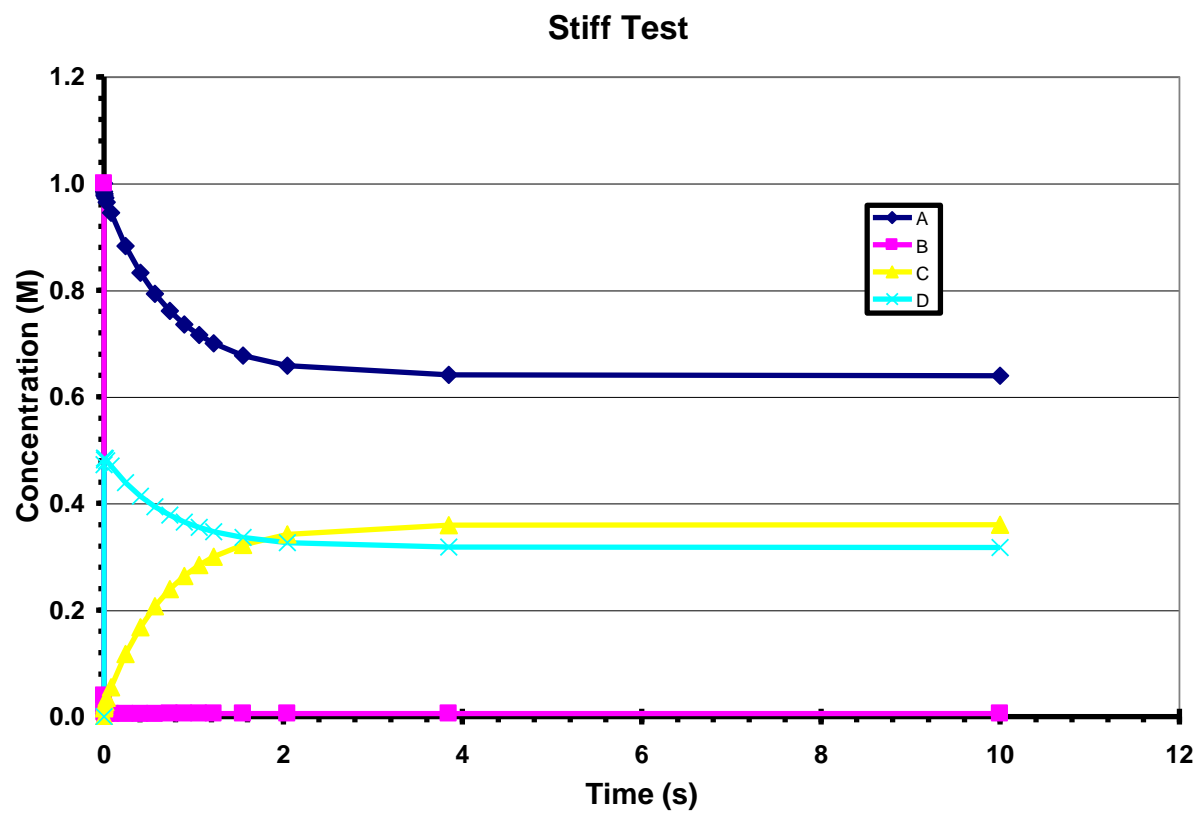
MODSTIF.TX2 - The kinetics reactions

SPECASTIF.TX2 - The species involved

PARMSTIF.TX2 - The parameters used

- A simulation run.

STIFF.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCASTIF.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 or Star-Office workbook: Oregonator_in_CSTR.xls and then clicking the **RUN** button located on the CONTROL worksheet.

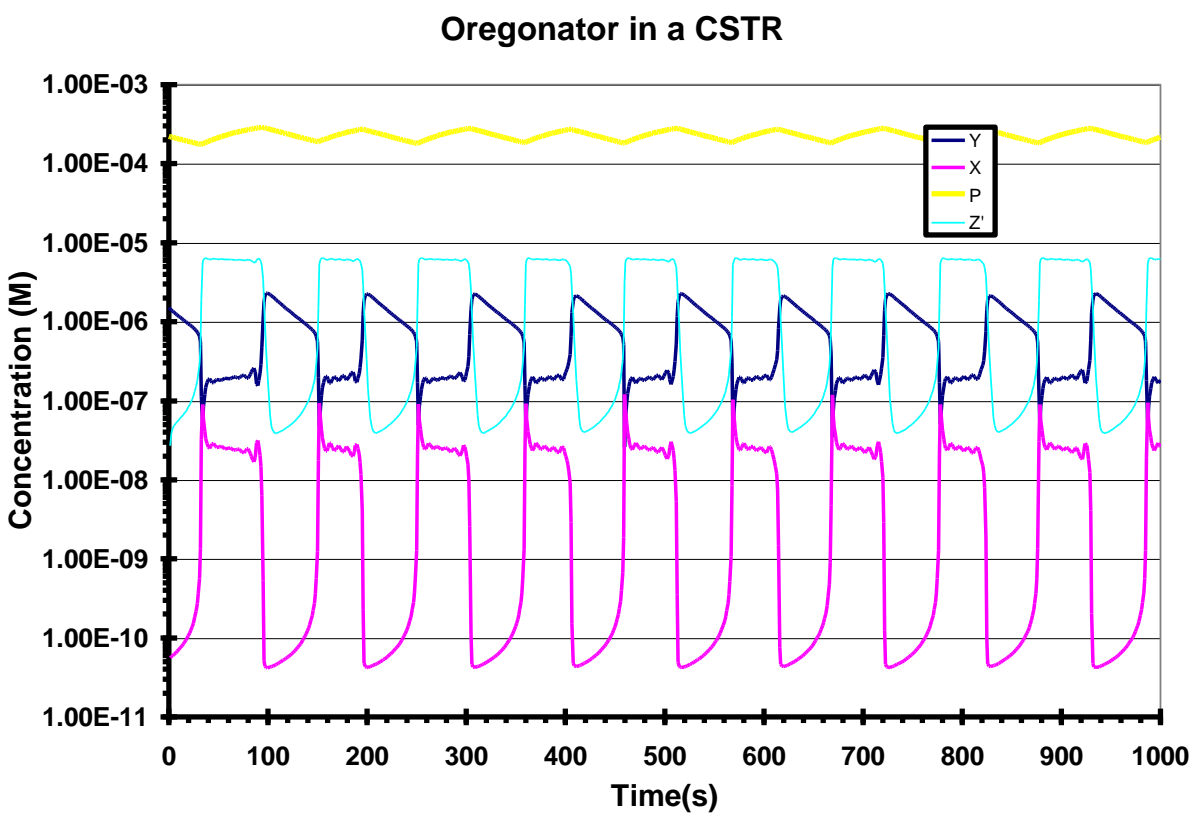
MODFORG.TX2 - The kinetics reactions

SPECFORG.TX2 - The species involved

PARMFORG.TX2 - The parameters used

CONCFORG.TXT - A simulation run.

OREGFLOW.BAT - A very simple 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 H₂ and O₂ 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 or Star-Office 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.

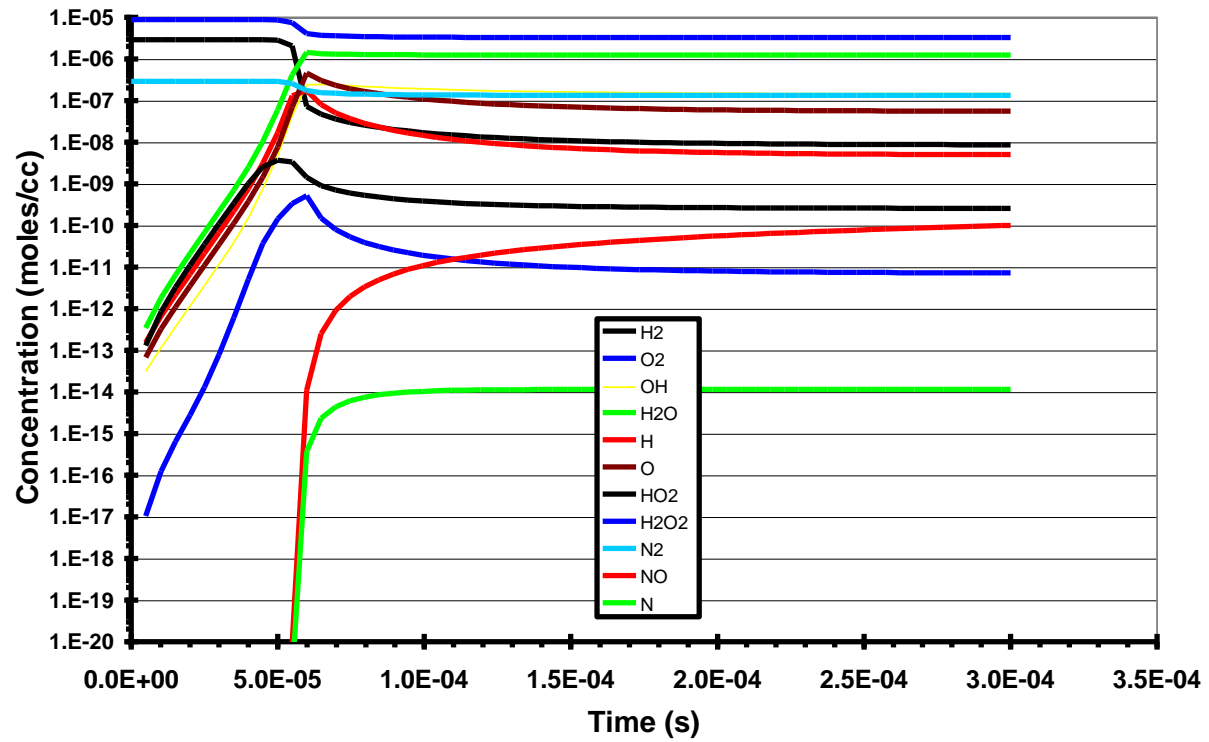
OH2.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCOH2.TXT.

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

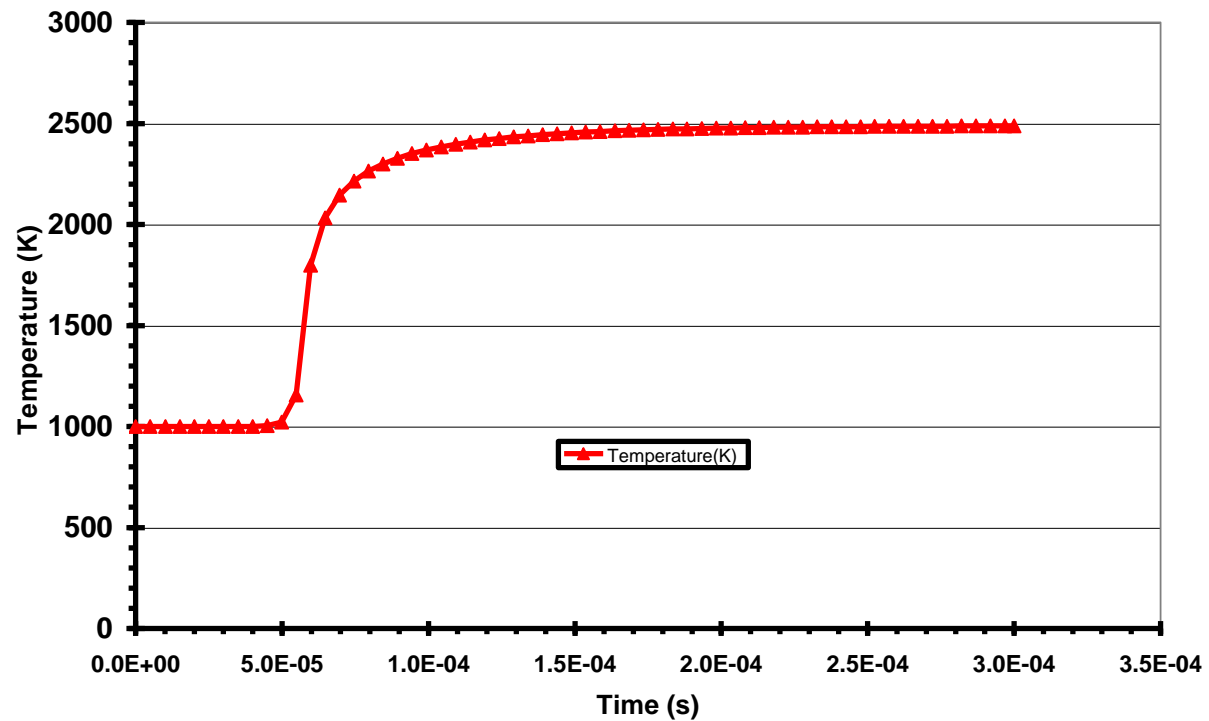
In addition, oh2f.bat uses the Chemkin thermodynamic database converted into **FREEFORM**! Examine the THERMFOH.DAT thermodynamic description spreadsheet.

Combustion of H ₂ and O ₂ at constant pressure						
Comparison of results at 3x 10 ⁻⁴ seconds						
	H ₂	O ₂	OH	H ₂ O	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 ₂ O 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



Combustion of H₂ and O₂ at constant pressure



GRI-Mech-3.0 Sample Runs

The GRI (Gas Research Institute)-Mech 3.0 mechanism is used by many research groups around the world 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 examine the following sample runs using GRI-Mech very closely. [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls and then clicking the RUN button located on the CONTROL worksheet.](#)

GRI-MECH RUN 4.0% CH₂O

The output concentration file, CONCHDK.TXT, matches the results by Hidka, et al [12] under the same conditions (4.0% CH₂O in Ar at 19.0 mole/m³ and T = 1805 K). [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls](#) and then clicking the **RUN** button located 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

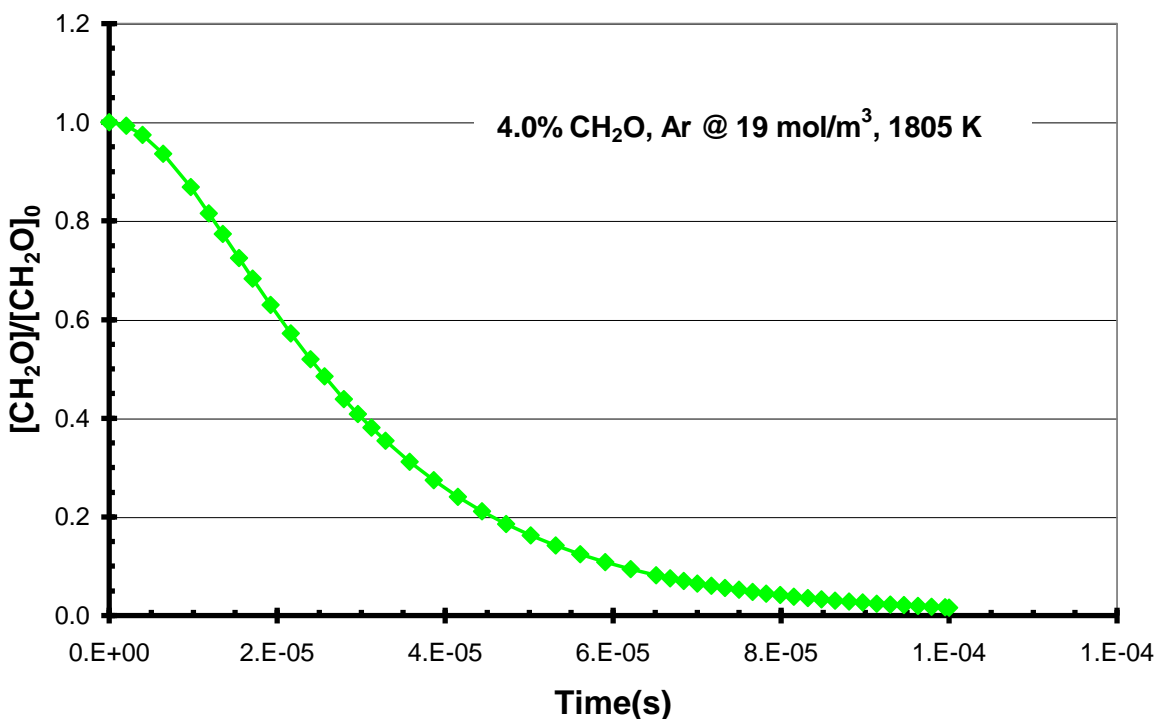
PARMHDK.DAT - The parameters used

THERMGRI.DAT - The thermodynamic description spreadsheet

CONCHDK.TXT - A simulation run.

grihdk.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCHDK.TXT.

GRI-MECH 3.0/CONCHDK.TXT



GRI-MECH RUN 1% CH₄ 3% O₂

The output concentration file, CONCV33.TXT, matches the results by Yu, et al [13] under the same conditions (1% CH₄, 3% O₂ in Ar at 1.58×10^{-5} mole/cm³ and T = 1856 K). [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls](#) and then clicking the **RUN** button located 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

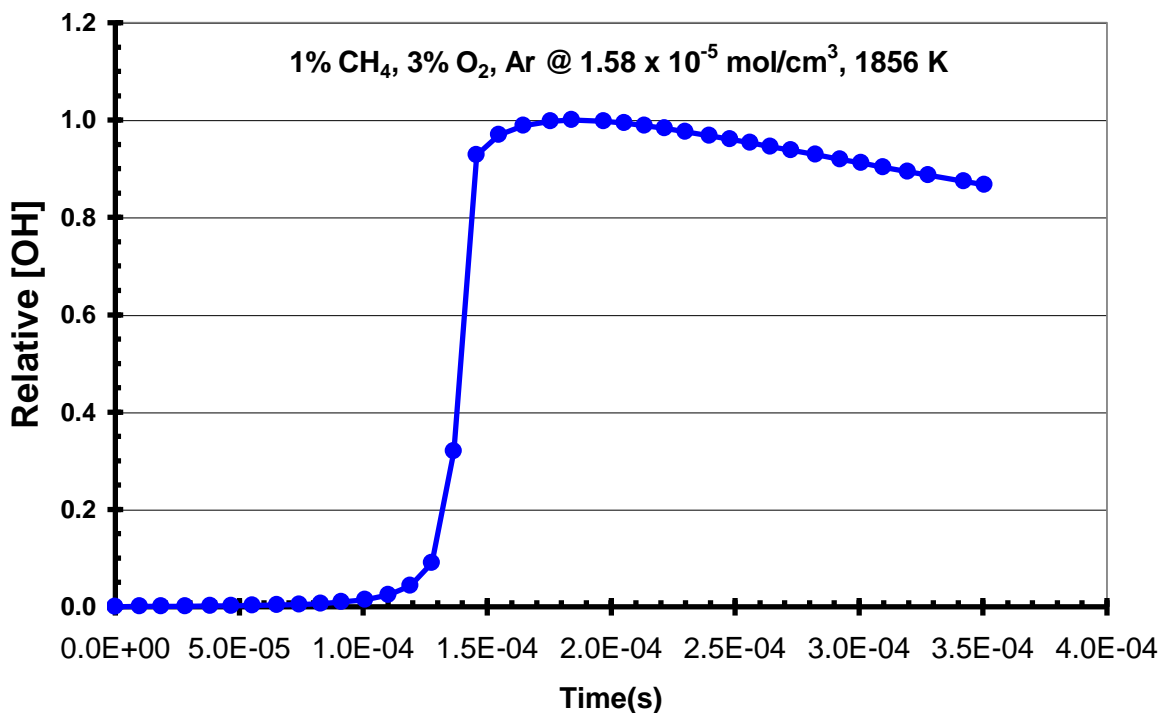
PARMV33.DAT - The parameters used

THERMGRI.DAT - The thermodynamic description spreadsheet

CONCV33.TXT - A simulation run.

griv33.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCV33.TXT.

GRI-MECH 3.0/CONCV33.TXT



GRI-MECH RUN 0.4% CH₄ 5% O₂

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 1.04×10^{-5} mole/cm³ and T = 1821 K). [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls and then clicking the RUN button located 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

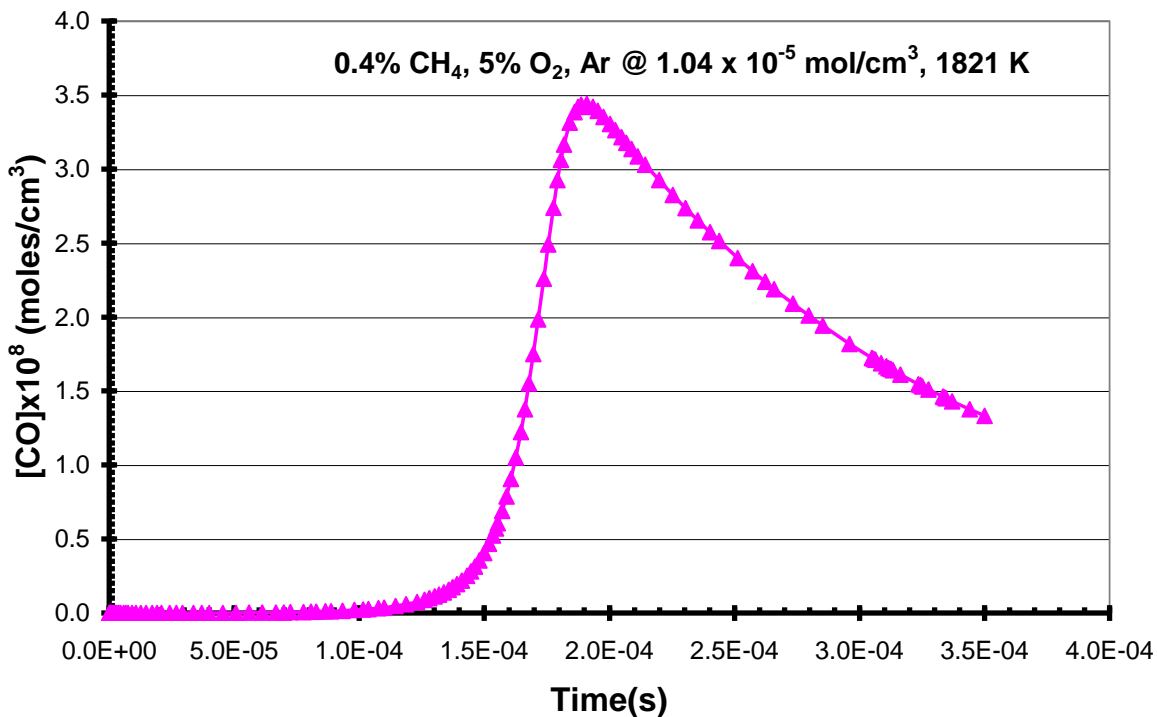
PARMV29.DAT - The parameters used

THERMGRI.DAT - The thermodynamic description spreadsheet

CONCV29.TXT - A simulation run.

griv29.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCV29.TXT.

GRI-MECH 3.0/CONCV29.TXT



GRI-MECH RUN 0.4% CH₄ 5% O₂

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 1.58×10^{-5} mole/cm³ and T = 1941 K). [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls and then clicking the RUN button located 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

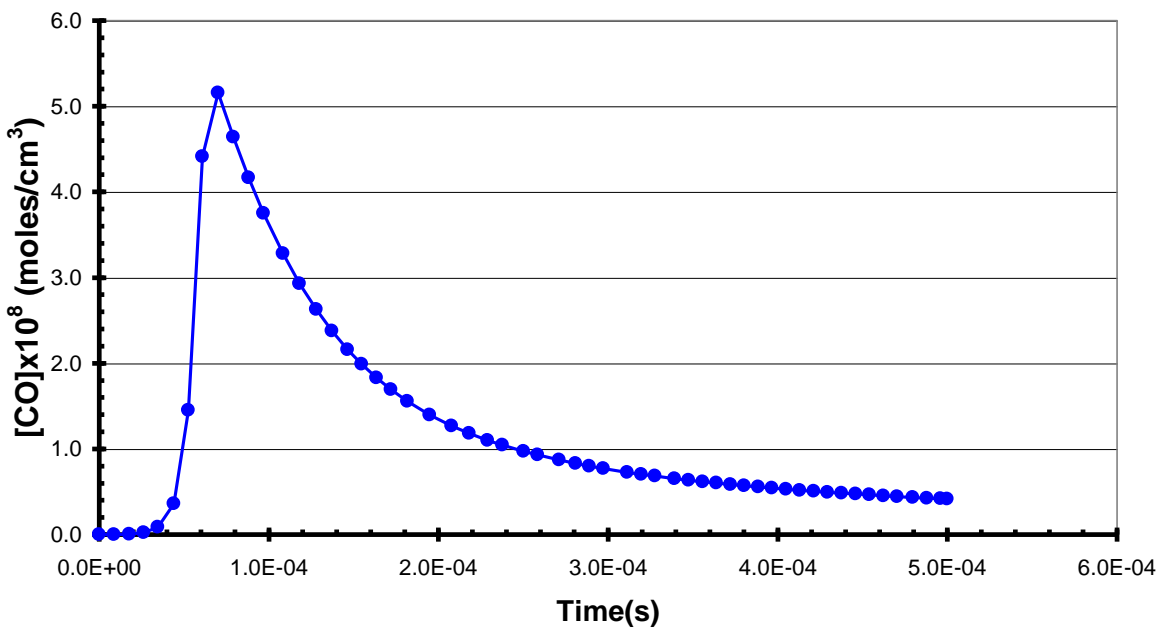
PARMV27.DAT - The parameters used

THERMGRI.DAT - The thermodynamic description spreadsheet

CONCV27.TXT - A simulation run.

griv27.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCV27.TXT.

GRI-MECH 3.0/CONCV27.TXT



GRI-MECH RUN 295 C₂H₆ ppm, 0.1055% O₂, 99.865% Ar

The output concentration file, CONCCT2.TXT, matches the results by Chang, et al [25] under the same conditions (295 C₂H₆ ppm, 0.1055% O₂, 99.865% Ar at 1.2 atm and T = 1794 K). [These models can also be executed by loading the Excel or Star-Office workbook: GRI_MECH_30.xls](#) and then clicking the **RUN** button located 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

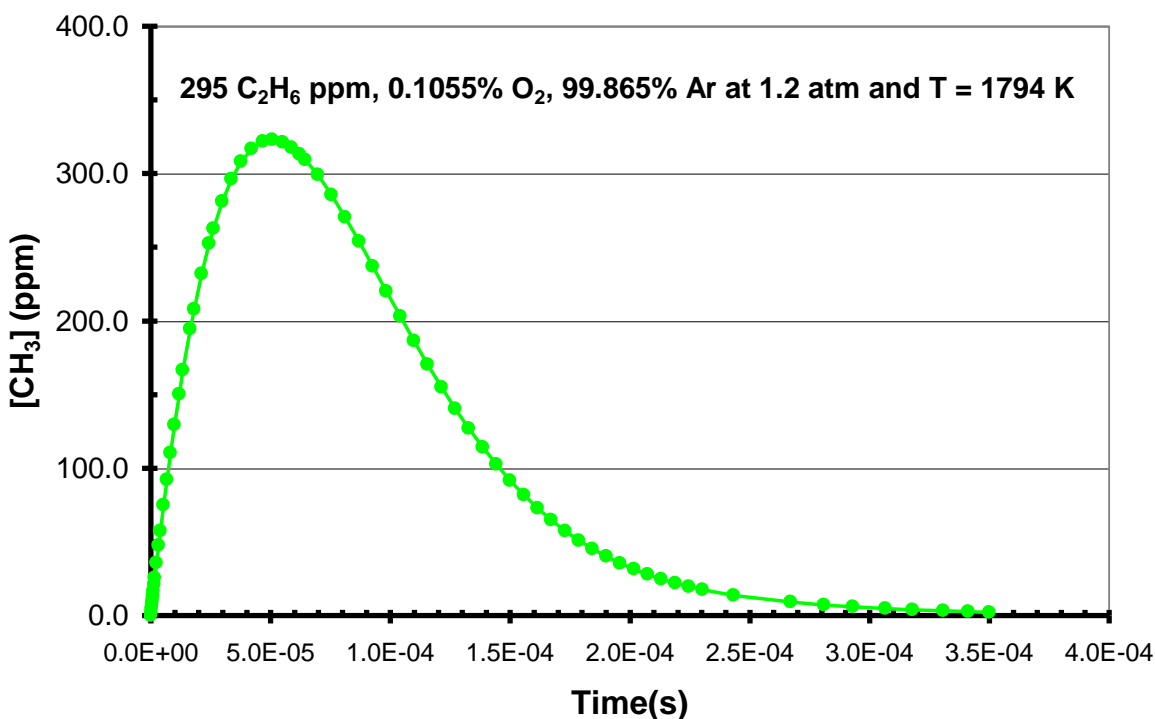
PARMCT2.DAT - The parameters used

THERMGRI.DAT - The thermodynamic description spreadsheet

CONCCT2.TXT - A simulation run.

grict2.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCCT2.TXT.

GRI-MECH 3.0/CONCCT2.TXT



GRI-MECH PISTON COMPRESSION RUN

This sample run shows one 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)

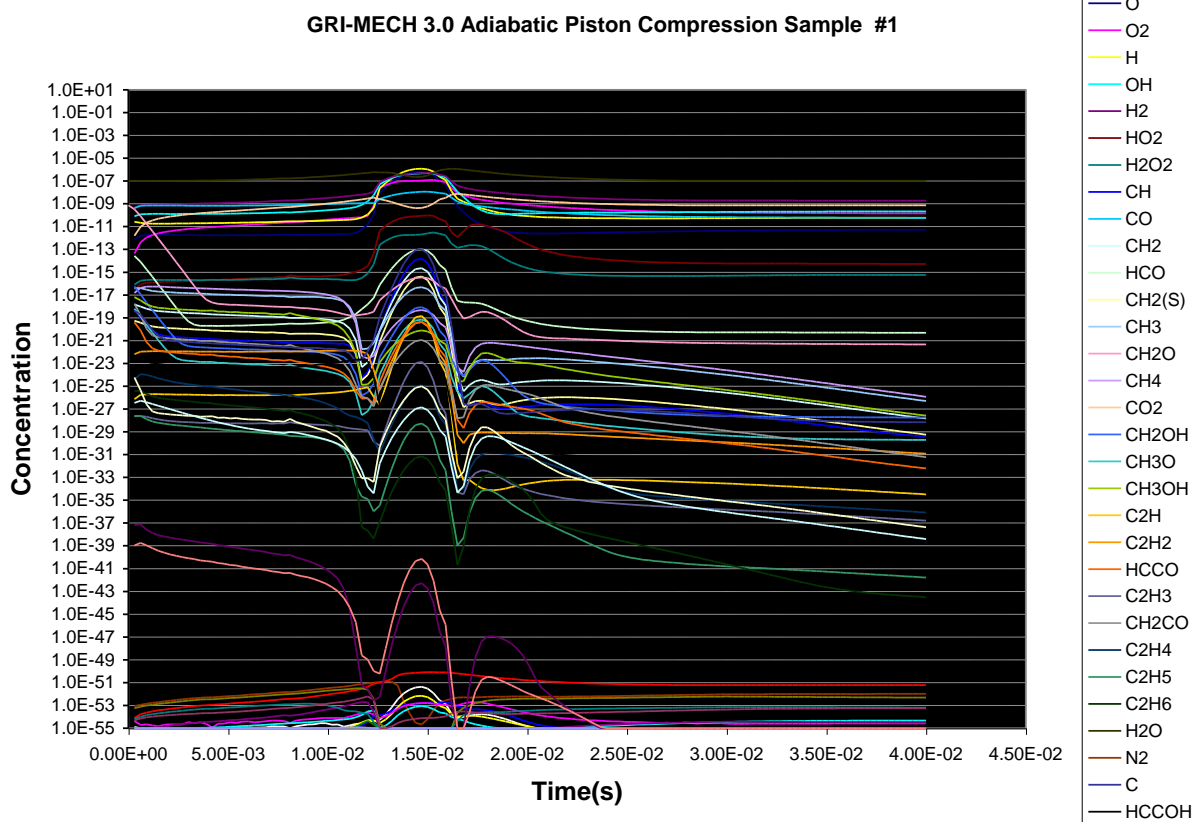
SPECPIST.DAT - The species involved

PARMPIST.DAT - The parameters used

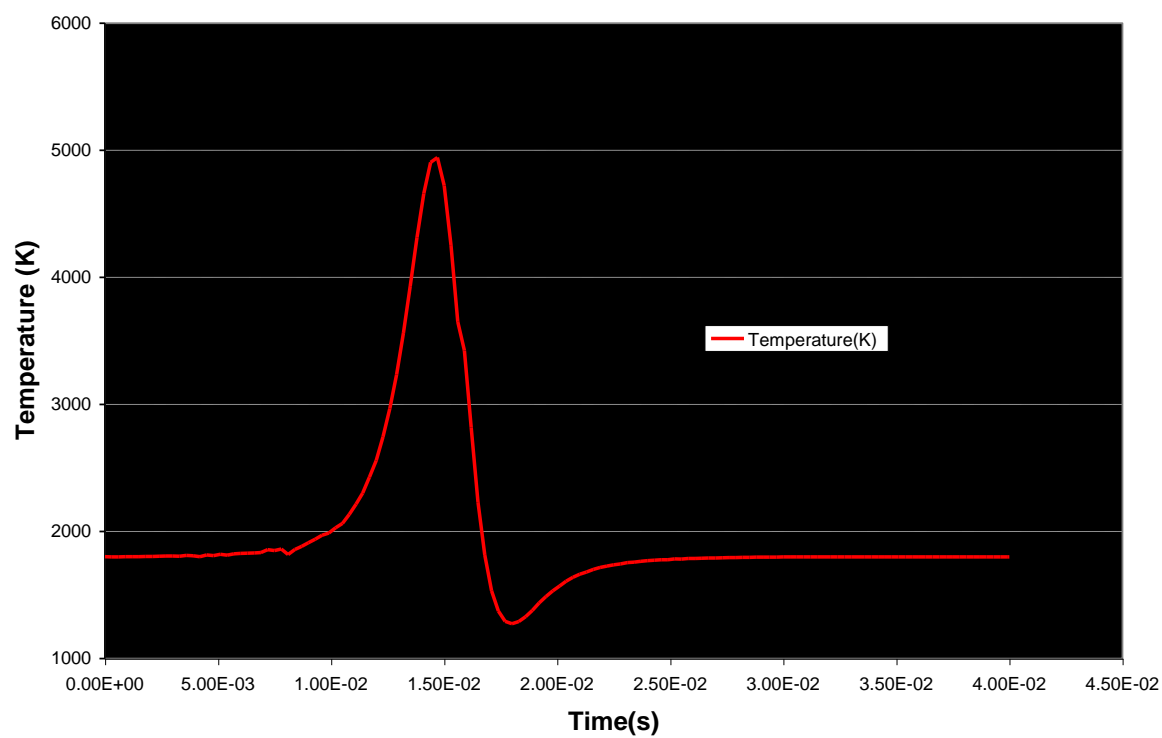
THERMGRI.DAT - The thermodynamic description spreadsheet

CONCPIST.TXT - A simulation run.

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



GRI-MECH 3.0 Adiabatic Piston Compression Sample #1



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 Star-Office workbook: Ethanol_Combustion.xls and then clicking the **RUN** button located 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:

$$\text{ignition_delay(sec)} = 1.0 \times 10(-14) \exp(15500 \text{ K/T}) [\text{C}_2\text{H}_5\text{OH}]^{-0.315} [\text{O}_2]^{-0.78} [\text{Ar}]^{0.259}$$

where the temperature is in Kelvin and all the initial concentrations are in moles/cm³.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)

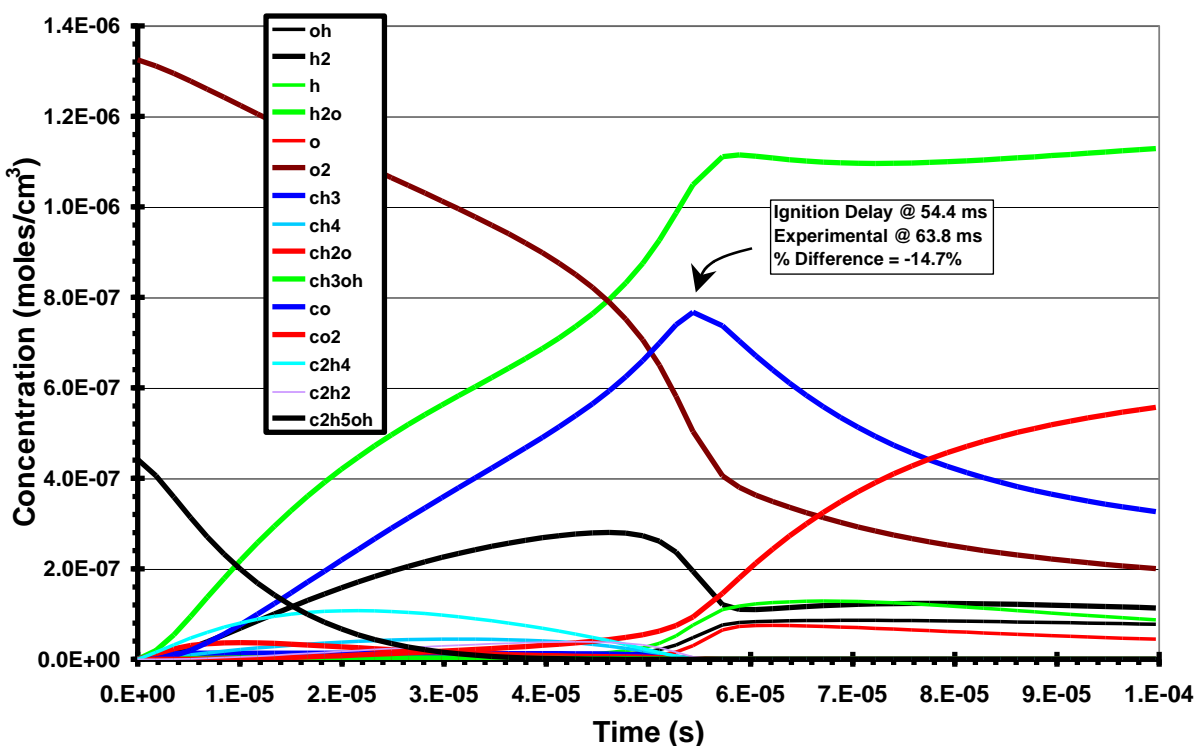
SPECETH1.DAT - The species involved / PARMETH1.DAT - The parameters used

THERMETH.DAT - The thermodynamic description spreadsheet

CONCETH1.TXT - A simulation run.

ETHANOL1.BAT - A very simple 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 Star-Office workbook: Ethanol_Combustion.xls](#) and then clicking the **RUN** button located on the CONTROL worksheet.

Combustion Run 1 of CH₃CH₂OH



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:

$$\text{ignition_delay(sec)} = 1.0 \times 10^{-14} \exp(15500 \text{ K/T}) [\text{C}_2\text{H}_5\text{OH}]^{-0.315} [\text{O}_2]^{-0.78} [\text{Ar}]^{0.259}$$

where the temperature is in Kelvin and all the initial concentrations are in moles/cm³.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)

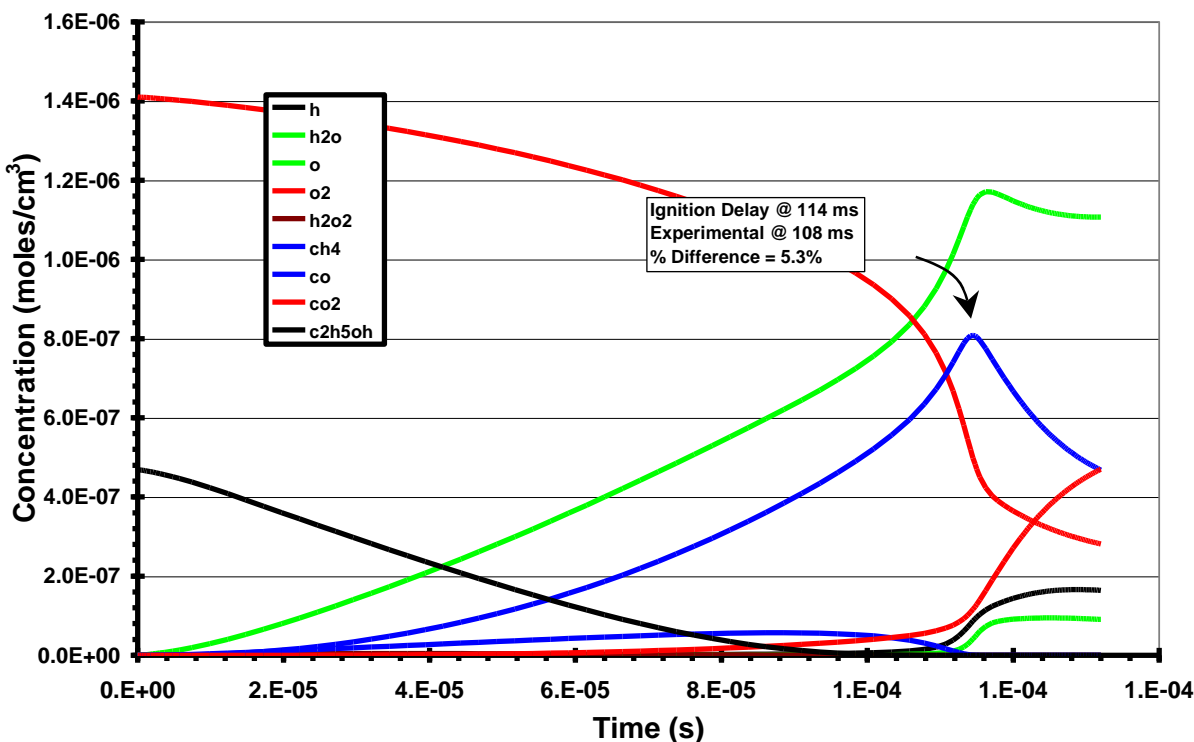
SPECETH2.DAT - The species involved / PARMETH2.DAT - The parameters used

THERMETH.DAT - The thermodynamic description spreadsheet

CONCETH1.TXT - A simulation run.

ETHANOL2.BAT - A very simple 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 Star-Office workbook: Ethanol_Combustion.xls and then clicking the RUN button located on the CONTROL worksheet.](#)

Combustion Run 2 of CH₃CH₂OH



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:

$$\text{ignition_delay(sec)} = 1.0 \times 10(-14) \exp(15500 \text{ K/T}) [\text{C}_2\text{H}_5\text{OH}]^{-0.315} [\text{O}_2]^{-0.78} [\text{Ar}]^{0.259}$$

where the temperature is in Kelvin and all the initial concentrations are in moles/cm³.

MODETH.DAT - The kinetics reactions (Converted from the Chemkin-II/III ethanol combustion model of Marinov [14] using the CK2KIN.EXE program)

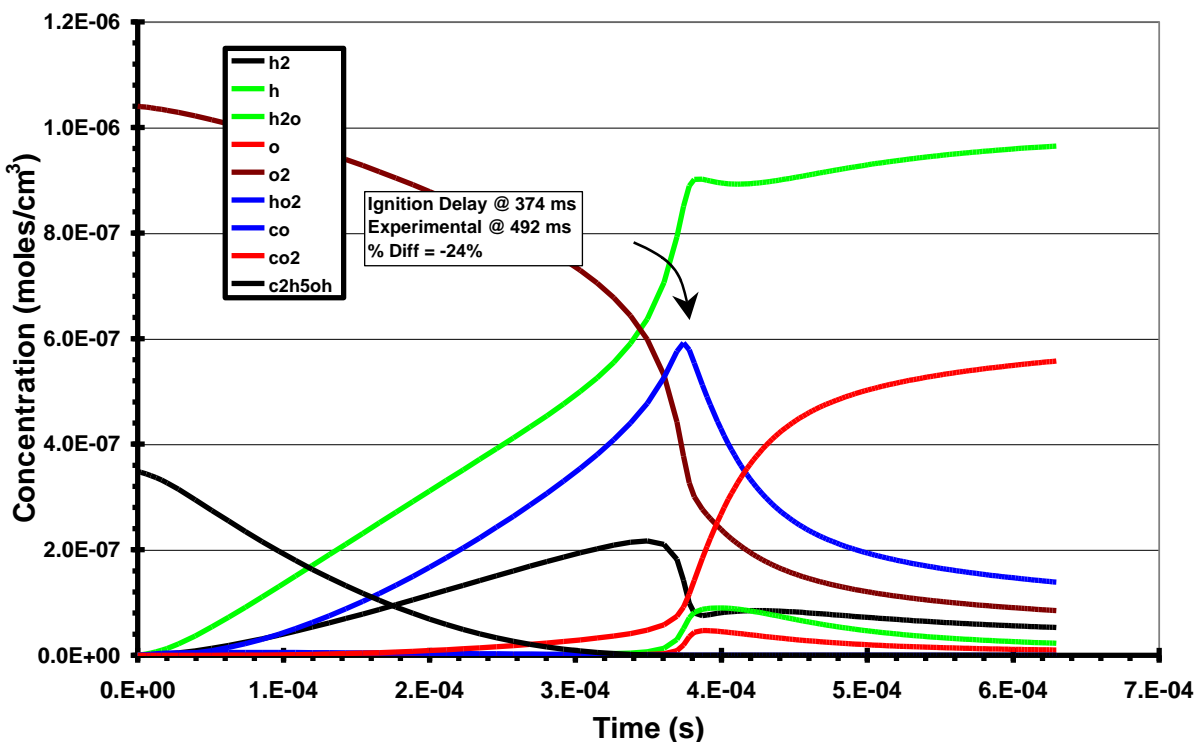
SPECETH3.DAT - The species involved / PARMETH3.DAT - The parameters used

THERMETH.DAT - The thermodynamic description spreadsheet

CONCETH3.TXT - A simulation run.

ETHANOL3.BAT - A very simple 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 Star-Office workbook: Ethanol_Combustion.xls and then clicking the RUN button located on the CONTROL worksheet.](#)

Combustion Run 3 of CH₃CH₂OH



Ozone Decomposition

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

MODOZO.DAT - The kinetics reactions

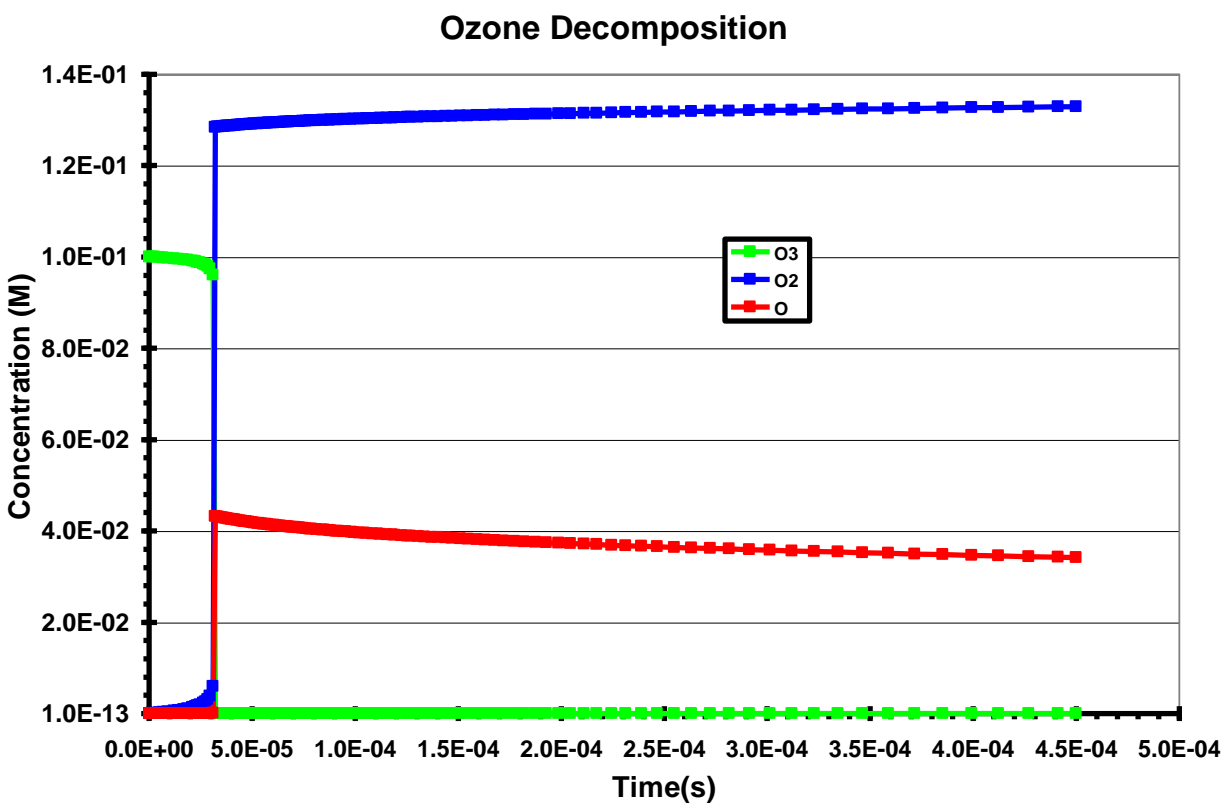
SPECOZO.DAT - The species involved

PARMOZO.DAT - The parameters used

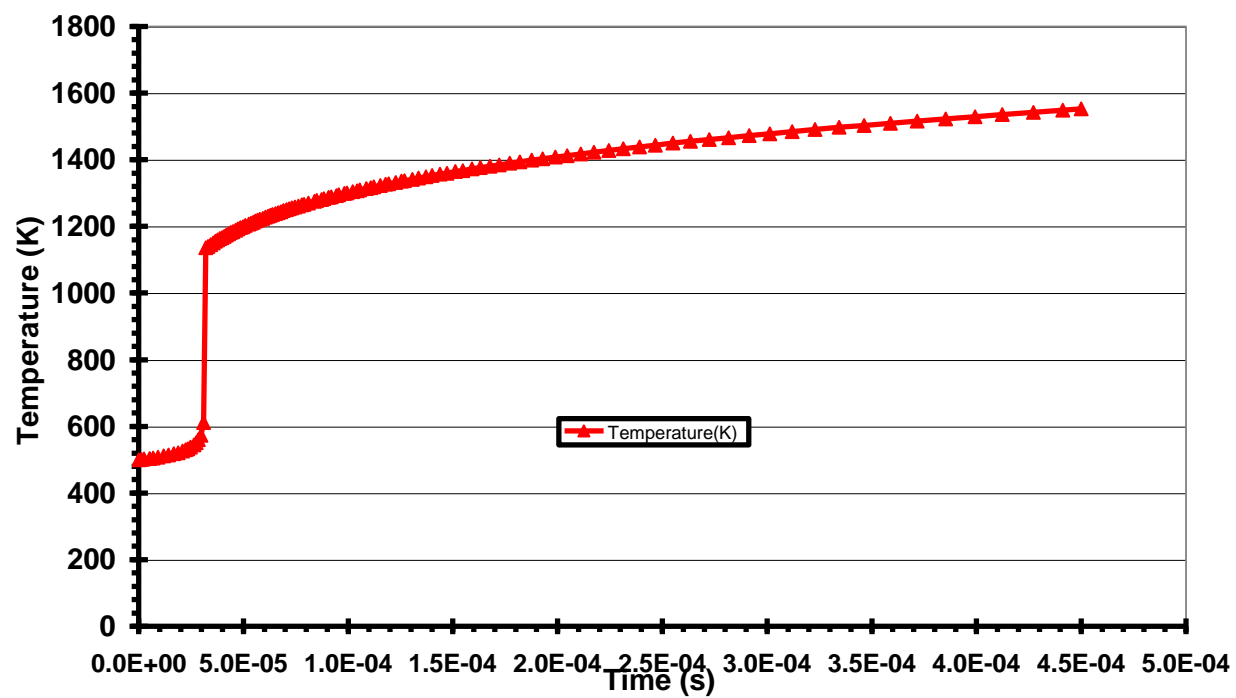
THRMOZON.DAT – The thermodynamic description spreadsheet

CONCOZO.TXT - A simulation run.

OZONE.BAT - A very simple one line batch file that will run the above model producing the concentration profile equal to CONCOZON.TXT.



Ozone Decomposition

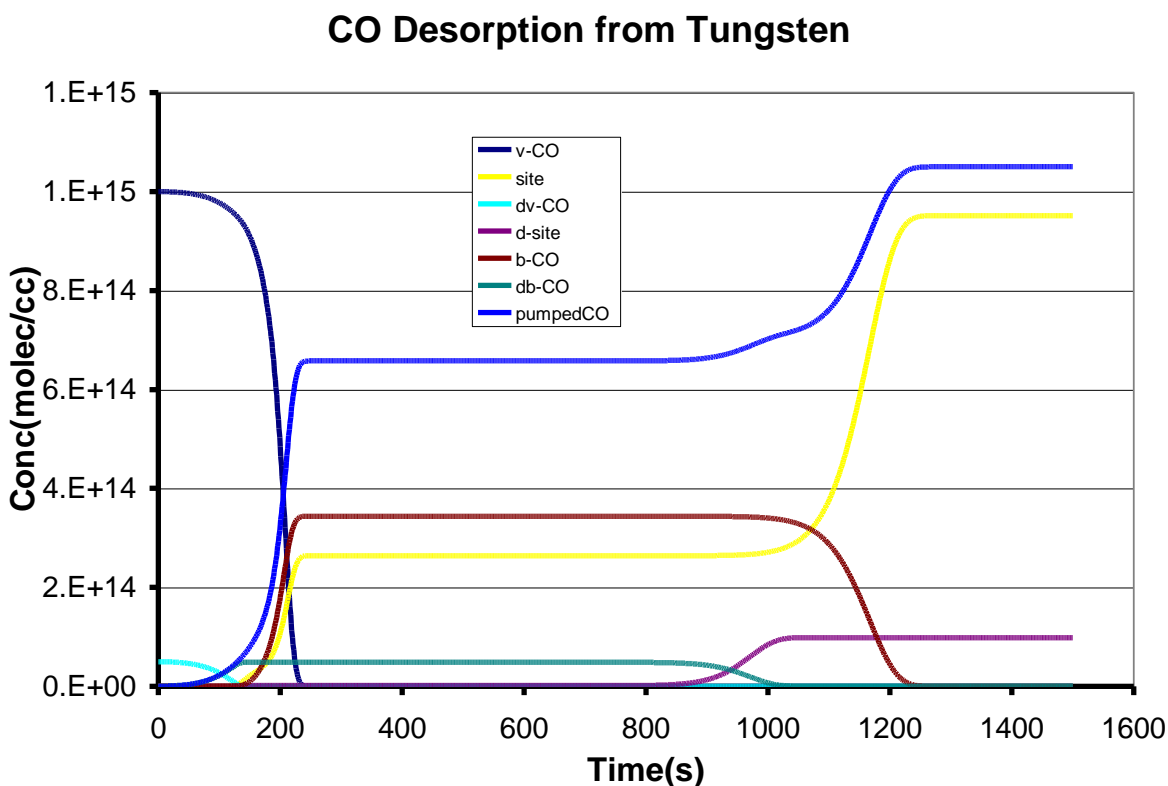


CO Desorption from Tungsten

The concentration output file, CONCWOLF.TXT, matches the plots in Houle and Hinsberg [16]. [These models can also be executed by loading the Excel or Star-Office workbook: Wolfrum_with_Temp_Program.xls](#) and then clicking the **RUN** button located 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 - A very simple 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 with those calculated by hand using the values from the CRC Handbook of Chemistry & Physics[18]. **This one line model also shows the use of 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 very simple 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 with those calculated by hand using the values from 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 very simple 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].

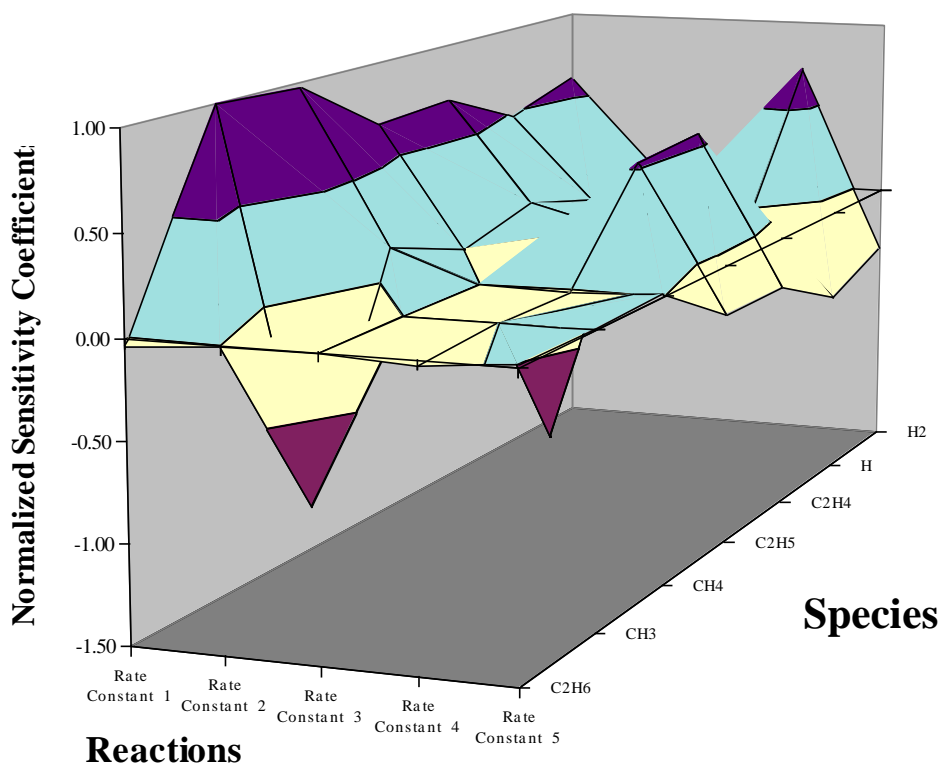
MODSEN1.TX2 - The kinetics reactions

SPECSSEN1.TX2 - The species involved

PARMSEN1.TX2- The parameters used

SENSIT1.BAT - A very simple 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

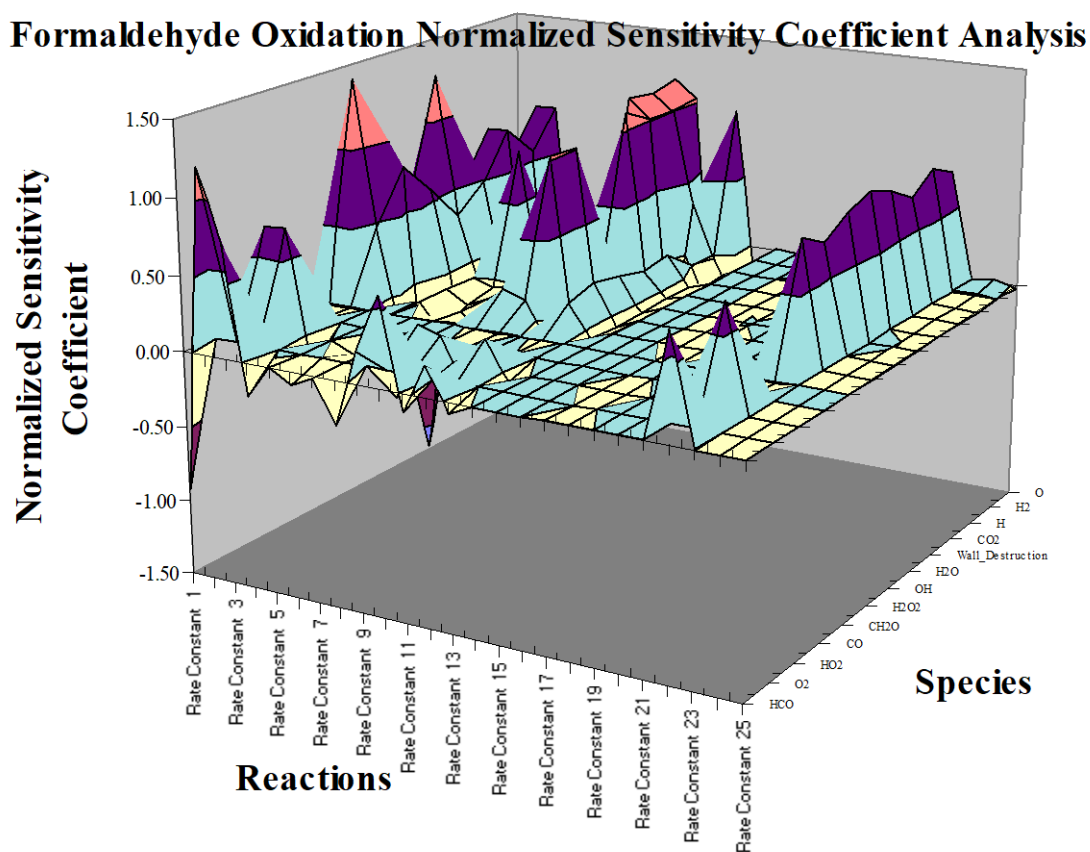
Output the sensitivity analysis file 2SENSIT1.TXT, which will match TABLE IV in the paper [8].

MODSEN2.TX2 - The kinetics reactions

SPECSSEN2.TX2 - The species involved

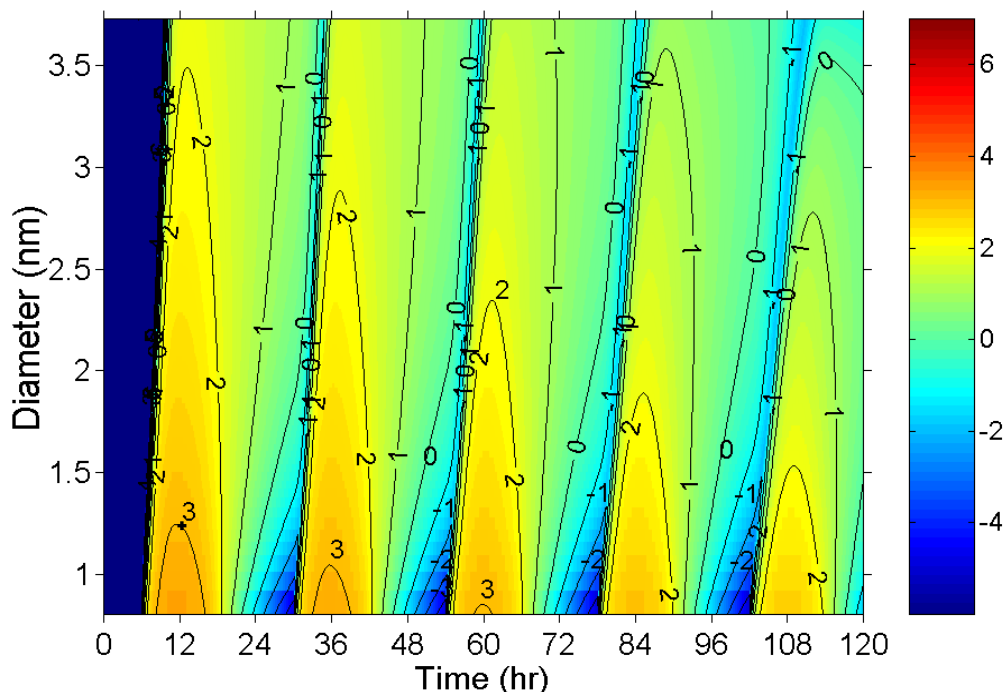
PARMSSEN2.TX2- The parameters used

SENSIT2.BAT - A very simple 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 running for **several days (that is simulation time, NOT REAL-TIME)!** The model and concentration files were not included because of their extremely large size. The author can provide these reactions upon request. The thesis chapter 8 explaining the contour plot below and their experimental comparisons is included with Kintecus. The chapter also contains many other large example 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, 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 which would minimize the presence of some harmful intermediate species, maximize certain valuable products, reduce/increase temperature and so on. Note that Kintecus will actually 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 fit the values against this interpolation. There is absolutely no need to “clean” your data, suggest interpolation methods nor specify timing meshes against your experimental data since Kintecus calculates values at exactly the times you specify in your experimental datafile. 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 with combustion/thermodynamics.

Kintecus V5.0 and up now supports **global data regression/fitting/analysis**. You can regress or fit or optimize multiple datasets that have multiple initial conditions such as temperature, pressure, concentration or any combination with data sets that have different time scales, different time steps, different species, temperature profiles, heat output, etc. 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

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

In addition to the sample batch files show in the table below, there should be sample Kintecus-Excel sheets showing various examples of fitting. On the Windows installation of Kintecus, there is a sub-menu called “Fitting-Regression” 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 H ₂ -O ₂ Combustion Reactions under Constant Pressure	Fitting several third-body rate enhancement factors against a dataset
FITTESTA.BAT	Optimization with 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	<i>Global data regression</i> /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 with the inclusion of 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	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. 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. Can be combined with fitdatan and initial conditions;however, FITLINK must be defined FIRST . See examples below	FITLINK FITLINK,fitdatan FITLINK,fitdatan,(filename to a text file that has initial conditions)	n/a
d	Tolerance	1 - 10 ⁻¹⁴	1 x 10 ⁻⁷ for Fitting Algorithms 1 and 3 1 x 10 ⁻⁵ for Fitting Algorithm 2
e	Maximum Iterations Allowed	1 - 2 x 10 ⁹	9000
f	Starting Vectors	1 x 10 ⁻¹⁰⁰ - 1 x 10 ¹⁰	1 x 10 ⁻³⁵
g	Starting “Temperature”	1 x 10 ⁻¹⁰⁰ - 1 x 10 ¹⁰	1 x 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 (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]. With each optimization algorithm, a user can choose from three comparison operators: 1=relative least squares, 2=standard least squares and 3=a proprietary function the

author has devised. The comparison operators compare the experimental/fabricated data and the simulated data and respond back to the optimizer with a number showing this difference. Once the user chooses a fitting/optimization algorithm and comparison operator, he must then supply the experimental or fabricated data in a text file named FITDATA.TXT. The default filename, FITDATA.TXT, can be change to a user-defined filename. The only requirements for the datafile is that “Time(s)” must be in the first column, first row, “END” must be in the first column last row, 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 lines by placing a “#” or a quote ‘ ’ as the first character on a line. If there is 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 datafile (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 numbers that are more accurate) to be performed. Conversely, increasing this value will cause less optimizations (shorter execution time but numbers that are less accurate) to be performed. It is very important to note that the tolerance is a minimum threshold needed to stop optimization when successive fits (compares between the data and simulated data) falls at or below this value. If the data and simulated data falls at or below the tolerance, the optimization will halt even if the data-simulated comparison is **terrible** (very large 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 that 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 fairly sensitive to the tolerance. It is suggested that you do not set a value above 1×10^{-5} . Setting smaller values (under 1×10^{-8}) can result in a substantial longer optimization run in some cases. Optimization algorithms #1 and #3 are more insensitive to the tolerance than the Powell 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 1×10^{-6} .

The Fit Switch Option **f** sets the starting vectors. The optimization of values, **N**, is actually 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”, 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. It is also the number of simulations to be performed before the data “temperature” is reduced by a percent represent 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 that Kintecus can fit data to. 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*)

What and How Can I Fit/Optimize ?

Selection of numeric parameters for fitting/optimization can easily 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 actually 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 located on the CONTROL worksheet.](#) (note the **extremely poor guesses**! But Kintecus actually obtains the exact answer that is **orders of magnitude away**!):

# Non-competitive Inhibition # of an enzymatic reaction	
# Example spreadsheet. 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!!	
1? E+S==>ES 1? ES ==> E+S	Equilibrium Constants 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, 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 amount of iterations. These values are also duplicated to the screen. In addition 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 $A = \epsilon \cdot l \cdot c$) from a series of absorbance values **or** a series of concentration values multiplied by some weight. A sample Excel Spreadsheet name [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:X1:Y1[:X2:Y2:X3:Y3:Xn:Yn]

Where X represents the column number in your fitdata file/worksheet and Y represents the starting weight guess. A very important note in 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 $(1/\epsilon \cdot l)$ 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) 1×10^{-9} and 5, while the fifth column has a starting weight of 0.09 and is constrained to stay between 1×10^{-4} and 1×10^{-1} .

Applying Constraints

A new feature in Kintecus V3.5 is the ability to apply 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 appear to 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 1×10^3** and **upper bound 1×10^7** .

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

Keep in mind that constraints can appear **anywhere**. One can select any numeric parameter to apply a constraint: 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. This 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 then 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 $E+S \rightarrow ES$ is the first reaction)

1.0e+8?	$E + S \rightleftharpoons ES$
k1*0.333333?	$ES \rightleftharpoons E + S$

If " $E+S \rightarrow ES$ " 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.

For more complicated constrained fits please see “**Global Data Fitting/Regressing with Multiple User Defined Constraints**” below. 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 the time of 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 . There is a sample Kintecus-Excel spreadsheet ([Enzyme_Regression_Fitting_WEIGHTS_TEST.xls](#)) demonstrating 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 and/or temperature that can be regressed against experiment data. This feature has many important uses in regression and data analysis. In this example, one is monitoring four wavelengths for absorbance, but each wavelength contains the absorbance from another species, so one cannot extract the concentrations from a kinetic one 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 is accomplished by utilizing the new “OUTC[.]” Special Species Directive Operator. This new species operators allows one to output a function of the species concentrations (or temperature) during a simulation run. The OUTC[] operator only allows summation, multiplication and negation. Summation is represented by a semi-colon, “;” 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, but 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. 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	Initial	Display Output	External	Species Special	Constant File?
#	Time in CSTR(s)	Conc.	(Y/N) ?	Conc.	Directives (/N)	(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 course of the simulation. For species A(S), Kintecus will output $300*[E] + 3700*[S]$, and etc. **Species that (a) have an OUTC[] function and are NOT part of a chemical reaction will only serve as an output function and NOT participate in any state calculation. Species that (b) have an OUTC[] function and ARE part of a chemical reaction will only serve as part of the rate calculation and will NOT participate in any state (system heat capacity, pressure, etc) calculation.** Those (a) species are only designed to be functions of other real, physical species present in your model. 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. There is a sample Kintecus-Excel spreadsheet (Enzyme_Regression_Fitting_Multi_Absorb.xls) demonstrating 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)

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.

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 that have multiple initial conditions such as temperature, pressure, concentration or any combination with data sets that have different time scales, different time steps, different species, temperature

profiles, weights, heat output, etc. Each dataset can be very different from each other. 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” upto “fitdatan.txt”. Kintecus will search in 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 of “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 as tab-delimited text files all those worksheets prefixed with “O_”.

Global Fitting/Regression with Multiple Initial Conditions

As mentioned above, one can regress or fit or optimize multiple datasets that have multiple initial conditions such as temperature, pressure, concentration or any combination. This is accomplished by providing a filename of tab/comma delimited text file 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 name of the species 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 that is 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 combustion experimental dataset.

One can now also regress/fit the initial conditions for a species (or temperature) in any of the initial_conditions.txt file. This can be done by suffixing any numeric value in an initial condition file with a question mark, “?”. Example, if the second data set had an unknown concentration of oxygen (using a guess of 2E19 molec/L) and a user wish 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)

Global Data Fitting/Regressing with Multiple User 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 "-FITL:2:2:FITDATAN,initial_conditions.txt" becomes "-FITL:2:2:FITLINK,FITDATAN,initial_conditions.txt". FITLINK must always be first and for plotting, one needs to use the latest Kintecus-Excel worksheets that have the latest VBA code embedded 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) to be computed between each iteration. You can use fairly complicated formats if you want, such as $k_1 = (\log_{10}(k_2 \cdot k_3 / k_4 + k_5) / (k_6 + k_9)) \cdot 0.5$ or fairly complicated linked parameters such as $E_6 = ((E_1 + E_2 + E_3 + E_4 + E_5) / 5 / k_2 + \log_{10}(\cos((k_3 + k_4) \cdot k_5)))$, 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 be sure to use this format: **kn**, **An**, **mn** or **En** where **n** is the reaction containing the rate 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. For example:

A23, m23, E23, T ; $k_{24} = A_{23} \cdot 1e-9 \cdot T^{m_{23}} \cdot \exp(-E_{23}/8.314 \cdot T)$

Or another example:

E19, E20, E21; $E_{24} = (E_{19} + E_{20} + E_{21}) / 3$

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]. See the Kintecus-Excel workbook

"Enzyme_Regression_Fitting_reverse_rate_fit_new_way.xls" as 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 compare with the experimental data. To fully explain all the output descriptors is beyond the scope of this document, but some of the more important 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 in 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 and there will be no standard deviations or covariance matrix that is outputted in the OPTOUT.TXT file.

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 though the output in [Appendix A](#) we see the title “START OF PREDICTION ANALYSIS” which signifies the beginning of residual analysis of your experimental data against the calculated data using the final fitted parameters. Some of the important 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), 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 has a Normal distribution and small magnitude relative to the data) a good numerical technique to quantify the normality of those residuals is the “Shapiro-Wilk W-test”. A 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 websource with full 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 the line, “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 use of the “-FITSTAT:BOOT” switch. There are additional options to 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 than the maximum amount of time for 100 optimization runs would require $20 \times 100 = 2,000$ 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 the parameter spreadsheet) just in case 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 change in accuracy to do before starting a bootstrap would be if your accuracy was 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 exact switches and including the “-rand” switch on the command line. The “-rand” switch will set all of Kintecus’ internal random number generators 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 extra switch will cause Kintecus to create the same exact bootstrapped errors on each machine!**

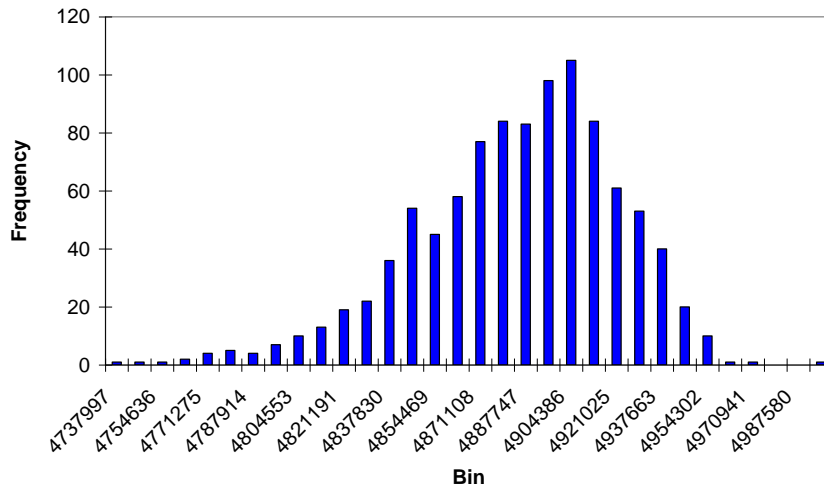
It is unlikely that the computers you run Kintecus on will have the same exact internal timings so the random number generators should produce different runs on each computer. Although Kintecus will report bootstrap errors in the OPTOUT.TXT file, those errors are for only the machine Kintecus was running. 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), then 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 respective 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. Shown below is a histogram plot of 1,000 bootstrapped runs of fitting the rate constants from the enzyme model. A sample Kintecus-Excel model spreadsheet that demonstrates bootstrapping on a simple enzyme model is included: “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, which is about 36.8 % and is the recommended value. You shouldn't have to change this value.

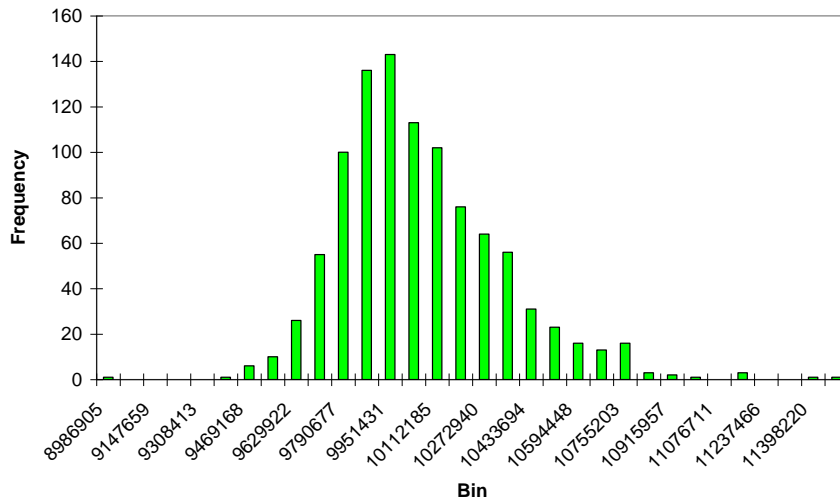
Shown below are the bootstrapped rate constants from 1,000 runs. The rate constants are fits to the model in the Kintecus-Excel Spreadsheet: “Enzyme_Regression_Fitting_BOOTSTRAPPING.xls”. Kintecus reports their average bootstrap values with bootstrapped standard errors as 4,880,502 +/- 36926, 1,0014,887 +/- 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.

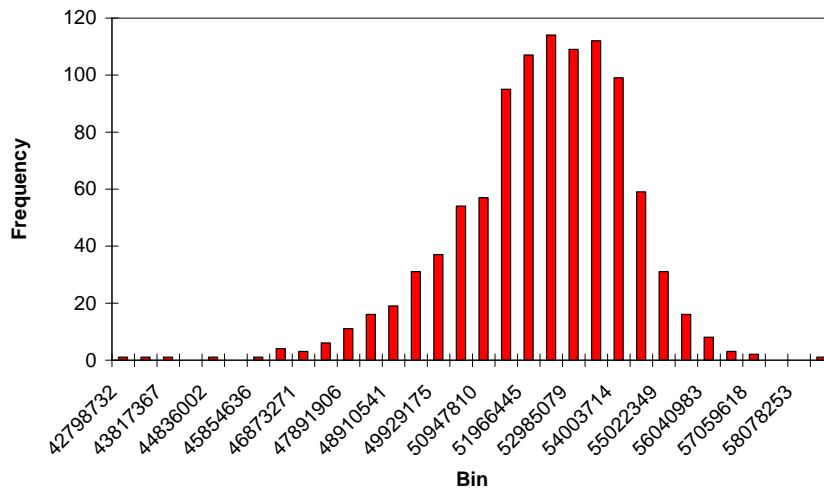
Rate Constant 1 Bootstrapped Values



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 also 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 a combustion model can be quite challenging. You will most likely get OVERFLOW ERRORS. This is due to the optimizer picking values that are making 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 end up with an accuracy in the range of 1×10^{-8} to 1×10^{-12} . 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**, ie.

`-THERM:THERM.DAT:FORCE` or `-THERM:D:FORCE`. This 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 try applying a constraint for the parameter you are trying to fit (see above on applying constraints).

Be Careful!

Just because you managed to get a great fit to your data and it passes every statistical test you can throw at it, the fitted values can be COMPLETELY WRONG! This can be especially true when you are fitting more than one value. For example, if a user tried to optimize all three expanded Arrhenius options at the same time 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 4.08×10^{14} ! Who's right? That depends on further molecular detail on 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? Maybe 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 the ability to detect 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 to be allowed in the Time(s) column of the experimental/fabricated data. If there are more, Kintecus will round your Times in the Time(s) column to six significant digits. If you really 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. Specifying a large number of significant digits can slow the fitting procedure tremendously and/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 Gibbs Free (or Helmholtz) energy of the system. The model spreadsheet file is no longer required. Only the species spreadsheet file and the parameter spreadsheet file are needed to run an equilibrium model. One does not even need to specify what species are products or reactants, just "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 advantages listed:

- No need to painstakingly create a kinetic model. This can take quite a while to do.
- Equilibrium models always finish completely. 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 completely, so you do not have a time profile evolution of the concentrations, temperature and other system values. This can lead to a few major problems:
- You do not know if a poisonous, dangerous or reactive intermediate grows to too large a concentration or the intermediate temperature may be too large/small or some other system value at a specific time.
- You cannot specify a loss/gain of mass, heat, phase/volume changes as the system runs to simulate real world conditions.
- Again, with no time profile of concentrations, one cannot maximize the concentration of a valuable product.
- It may take forever to get the final state of the system, but you will never know how long 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 [The Thermodynamic Description Spreadsheet](#) or enter a “D” to use the default Thermodynamic Description Spreadsheet name of “EQTHERM.DAT”. Option “b” is only useful if you are applying perturbations on 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 much faster solution times for constant temperature runs, but sometimes can “hop” over the correct solution and end in a not-so-correct solution. A good example is the H₂SO₄ 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, but 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 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, and 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” (Default=75) has been reached. If the “Maximum number of non-linear solver tries” is reached 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 who is having problems with the time to finish a final equilibrium run or to 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 to decrease the computational time to arrive to 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”, ie. “-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.](#)

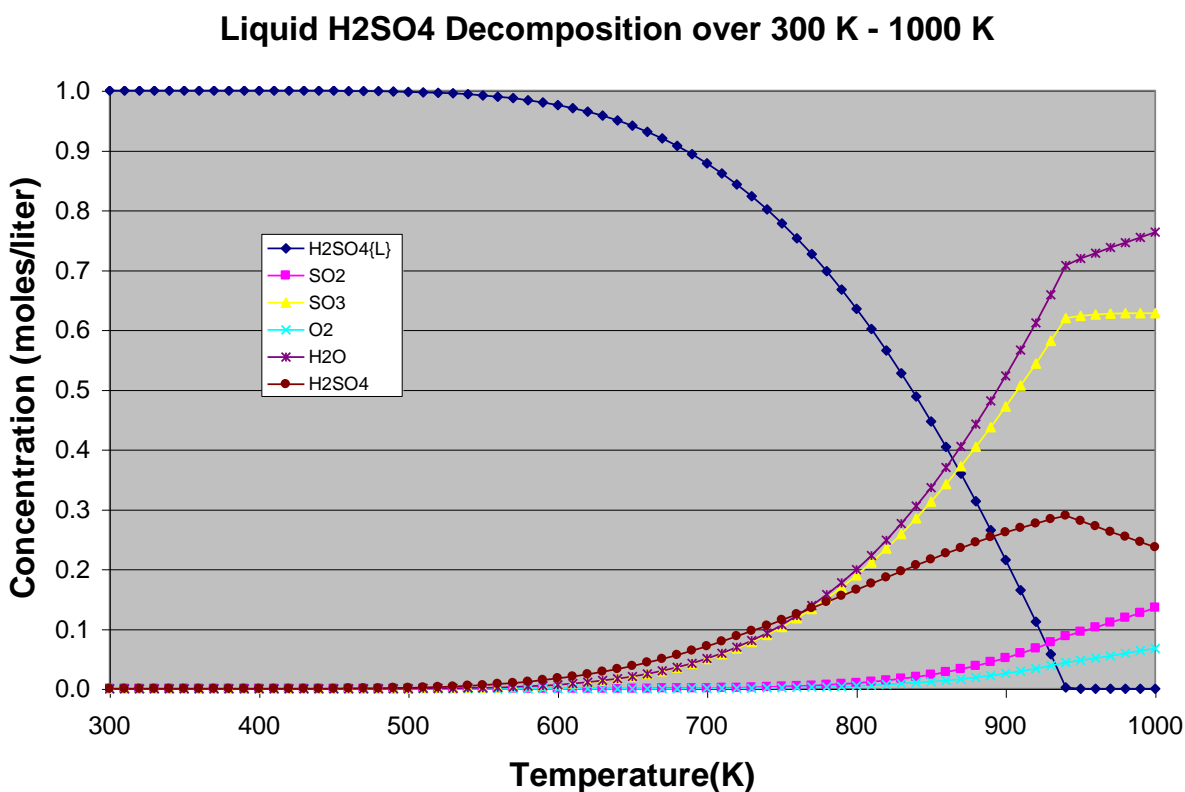
Batch File	Type of Equilibrium Run	Conditions
EQUIL1.BAT	Propane-Air Combustion	Constant Temperature Constant Volume
EQUIL2.BAT	H ₂ -O ₂ Combustion	Constant Temperature Constant Volume
EQUIL3.BAT	Propane-Air Combustion	Constant Temperature Constant Pressure
EQUIL4.BAT	H ₂ -O ₂ -N ₂ Combustion	Constant 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 H ₂ O ₂	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 H ₂ SO ₄ 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
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Table 15. Various sample equilibrium runs located in the ./Kintecus/EQUIL/ subdirectory.

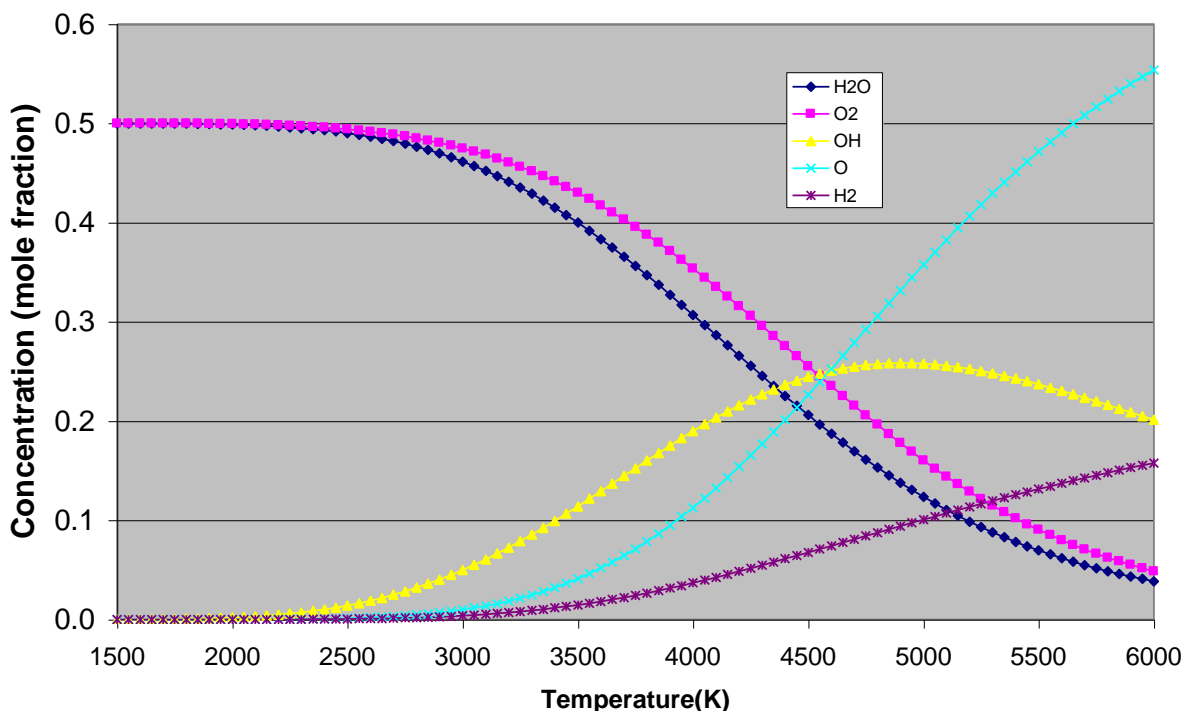
Sample Equilibrium Run Plots

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 shows 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 equiliba.bat file located in the /EQUIL/ subdirectory).

O2-H2 Decomposition Over 1500 K to 6000 K



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 a number of people that think Kintecus' Equilibrium mode is sometimes yielding 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 takes into account of ALL chemical paths that can possibly exist for ALL species. For a closed, adiabatic chemical kinetic reaction system to yield the same exact results, ALL CHEMICAL PATHS must exist. Let me repeat that, **CHEMICAL KINETIC PATHS MUST EXIST BETWEEN ALL SPECIES FOR THE SYSTEM TO EQUAL TRUE EQUILIBRIUM RESULTS AT INFINITE TIME.** Now in reality, some reactions might never happen due to such large reaction barriers that infinite time extends beyond the end of time of the known universe, but 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 very simple example to demonstrate this:

1) There is a one-line sample reaction of
 " 2 butene = cis2-buten + t-butene with constant temp. at 298K " that is 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). Noticed 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, simply 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.

To make this clear for you ILDM people, please keep in mind that Kintecus' Equilibrium mode does not give you the reaction equilibrium ($df/dt=0$), but the TRUE equilibrium (global minimum of $dG/dx=0$). 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 $df/dt=0$ (its 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 are controlling the concentration and temperature profiles. A good analogy would be a hurricane forecaster that only shows one single 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 as well as possible maximum and minimum time profiles concentrations (and temperature) can take on during the course of all the simulations.

Uncertainty analysis/confidence band predictions and the related can now be calculated in Kintecus V3.7. Kintecus V3.7 now incorporate uncertainty analysis with an extremely versatile, easy and quick way 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 very easy, straightforward manner with the standard deviations and/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 also be displayed and plotted. There are two sample Kintecus-Excel spreadsheets that you may wish to examine: “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 all optional, but when setting options b to g all preceding options must be specified. 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 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 1/100 change

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 and all 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 and all 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 up the type numbers for the sets you wish to randomize. 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 just enter “12” (8+4) for option “b”. **[31]. You can selective 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 1 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, \bar{x} 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 to 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 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
BOUND or BOUNDC	External Concentration for Species
TEMP or TEMPERATURE	Initial Temperature
EXTERNTMP 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 as option “e” with the exception 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: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 in that the value you give represents **one sigma**, there is about 1/100 chance probability that a value that is **three times greater** than the relative standard deviation you give will be selected. You should stay away from 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, residence times. In uniform distributions, the relative standard deviation you give 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 overridden 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 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 dictate 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.

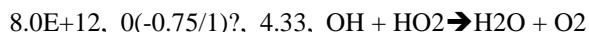
For example, for the reaction of $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$, if we assume the rate constant was $8.0 \times 10^{12} \pm 2 \times 10^{12}$ (assuming 2×10^{12} represents **one-sigma!**) then the relative standard deviation is 20% or **0.2**. This reaction can be written in the model spreadsheet with an uncertainty override and assuming a **Gaussian distribution** (specified by the number “**1**” after the slash “/”):



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 then it is NOT INCLUDED in the uncertainty analysis. For some parameters this makes sense such as initial concentrations, residence times, external concentrations, but for a few (like the exponent **m** for T^m in the expanded Arrhenius equation) in which 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 by specifying a negative value instead of a relative standard deviation for the first value. The negative value is actually the ABSOLUTE RANGE for the spread of the random number. For example:



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 selected. If the -0.75 were a $+0.75$, then there would be no change during ALL uncertainty runs for $m=0$ because $0 \times 0.75 \times (\text{random number})$ 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 always named **CONCAVG.TXT**, **CONCSTD.TXT**, **CONCMAX.TXT** and **CONCMIN.TXT** and should be located in the same directory as Kintecus.exe. 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 and 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 you are using the latest Kintecus-Excel spreadsheets! This is very important!

Some Examples!

The first example implementing an uncertainty analysis run is with 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 great concentration variations of over 1,000% (!!!) for [S] and [ES] about the time of 900 seconds. If [S] or [ES] were dangerous, poisonous intermediates, figure 15 demonstrates that exact control of some initial conditions are required. All is not lost as the final, equilibrium concentrations of all species are all very close.

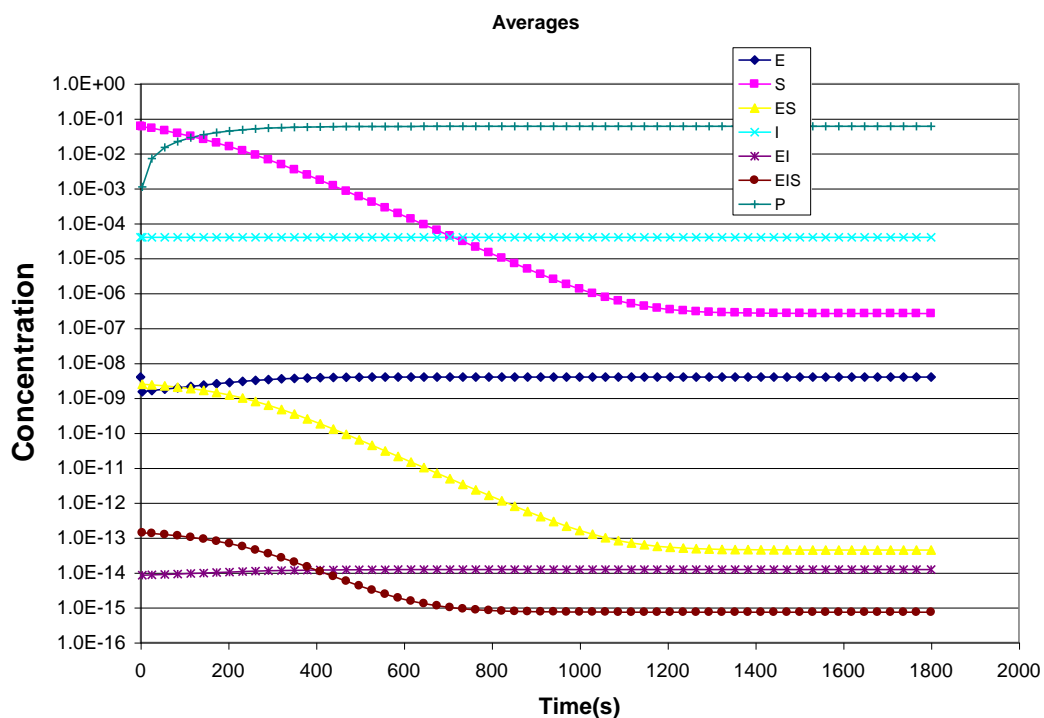


Figure 15. Plot of an enzyme model utilizing one single run. The y-axis is logarithmic.

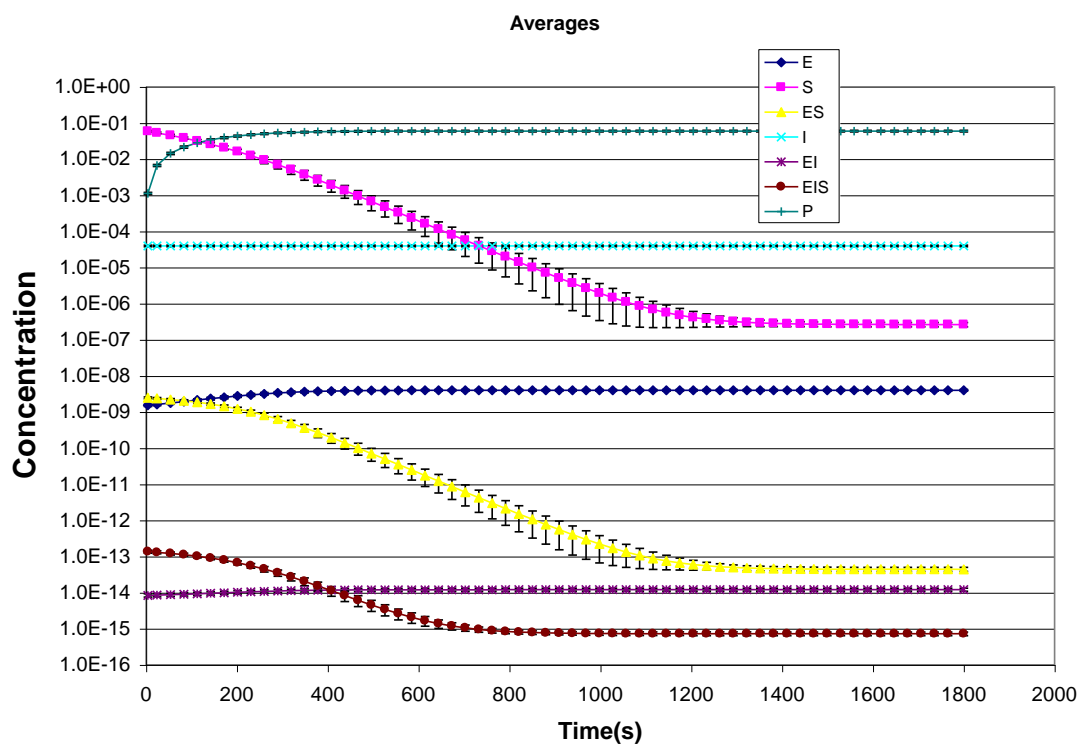


Figure 16. An average plot with one-sigma deviations of an enzyme model utilizing 100 single runs in a Kintecus uncertainty analysis run. The y-axis is logarithmic. Note the great concentration variations of over 1,000% (!!!) for [S] and [ES] about the time of 900s.

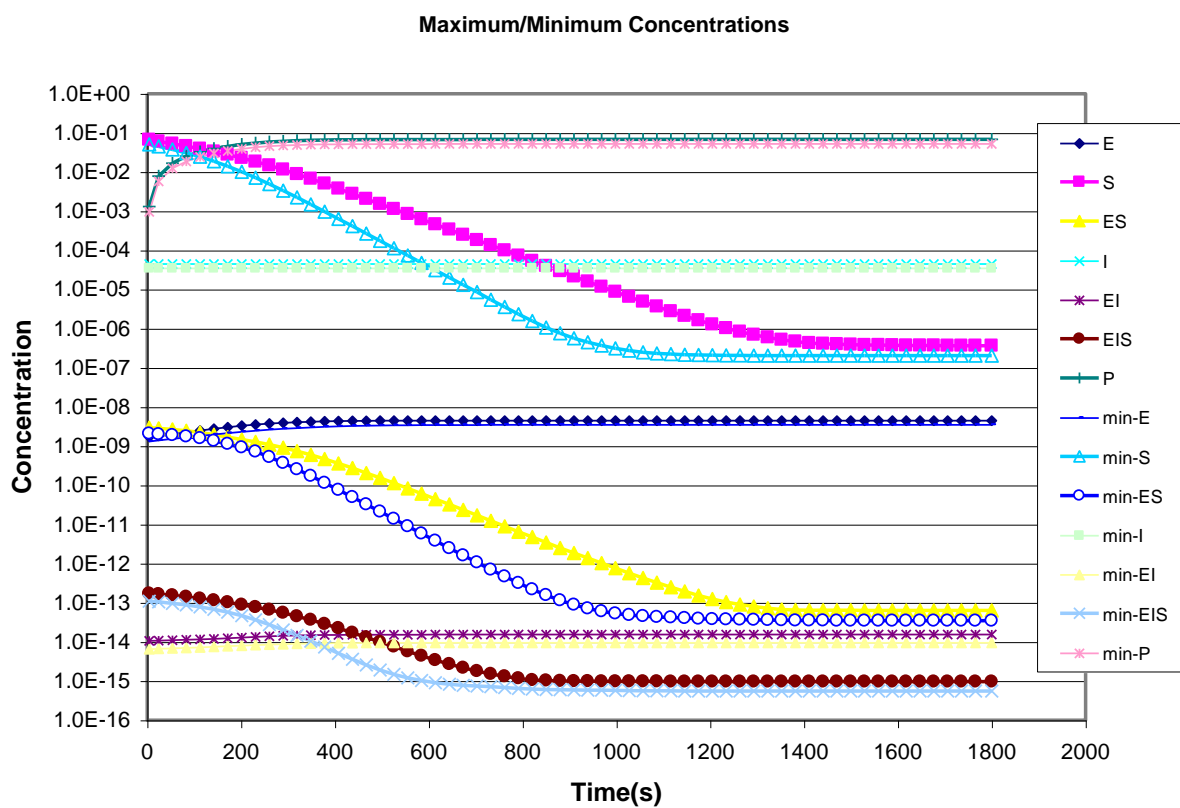


Figure 17. Maximum/minimum of an enzyme model utilizing 100 single runs in a Kintecus uncertainty analysis run. The y-axis is logarithmic. Only the species S and ES show great concentration ranges under the uncertainty analysis, but, the final equilibrium concentrations show little changes.

The second example applying uncertainty analysis is with 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 clearly see that the average does differ significantly from the single run, with the concentration profile of O₂ containing the greatest scatter. Figure 22 shows a zoom 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, constant pressure. These average concentrations are close to the concentrations in figure 21 that were generated from single-run using nominal initial conditions, but there is a great intermediate variation in the concentration time profiles. Interestingly, the concentration of H₂O₂ around 1.9x10⁽⁻⁴⁾ seconds shows very little scatter indicating that at this time point, [H₂O₂] is quite invariant to the accuracy of rate constants, thermodynamics, third-body reaction enhancements and even initial concentrations!

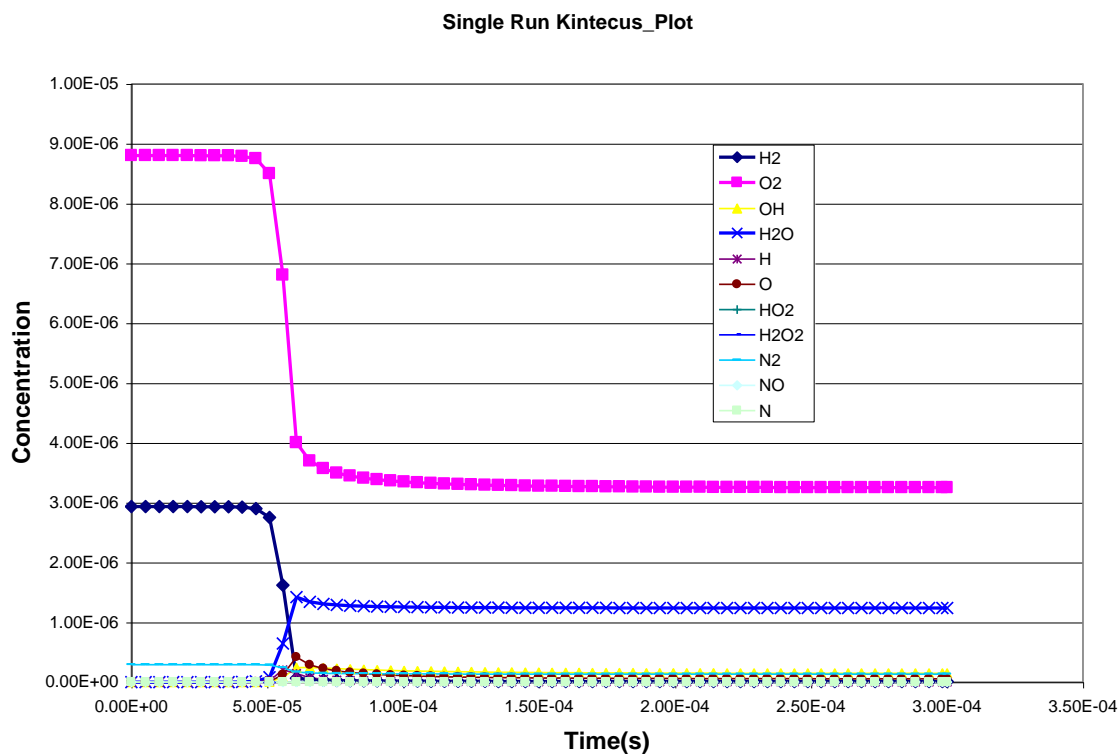


Figure 18. Concentration profiles from a single run of the combustion of H₂ and O₂ at constant pressure.

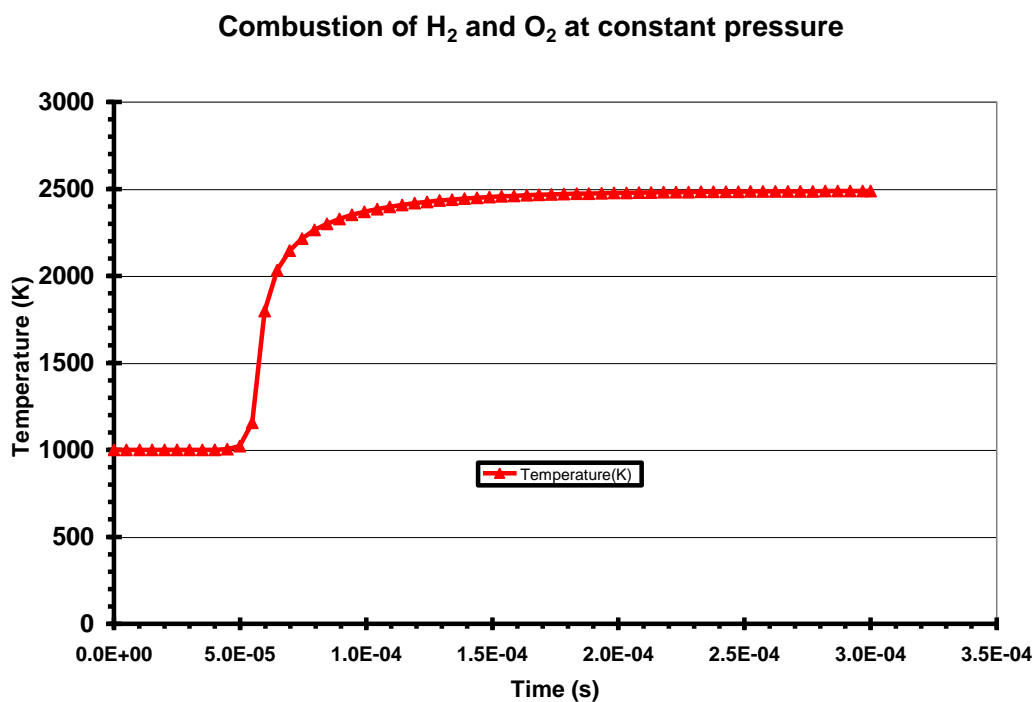


Figure 19. Temperature profile from a single run from a single run of the combustion of H₂ and O₂ at constant pressure.

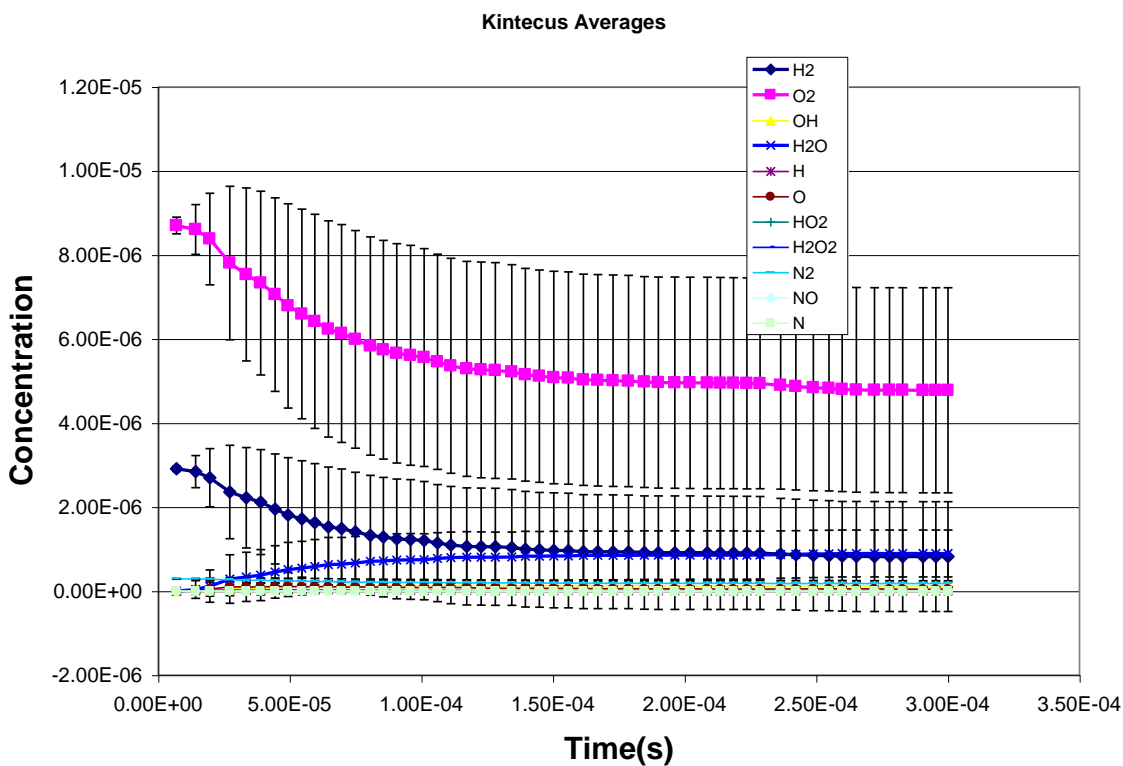


Figure 20. Average concentration profiles from the H₂-O₂ combustion run under constant pressure with error bars from 100 sample runs with “-CONF” switch. These average results are very much different from the single run shown in figure 17 above!

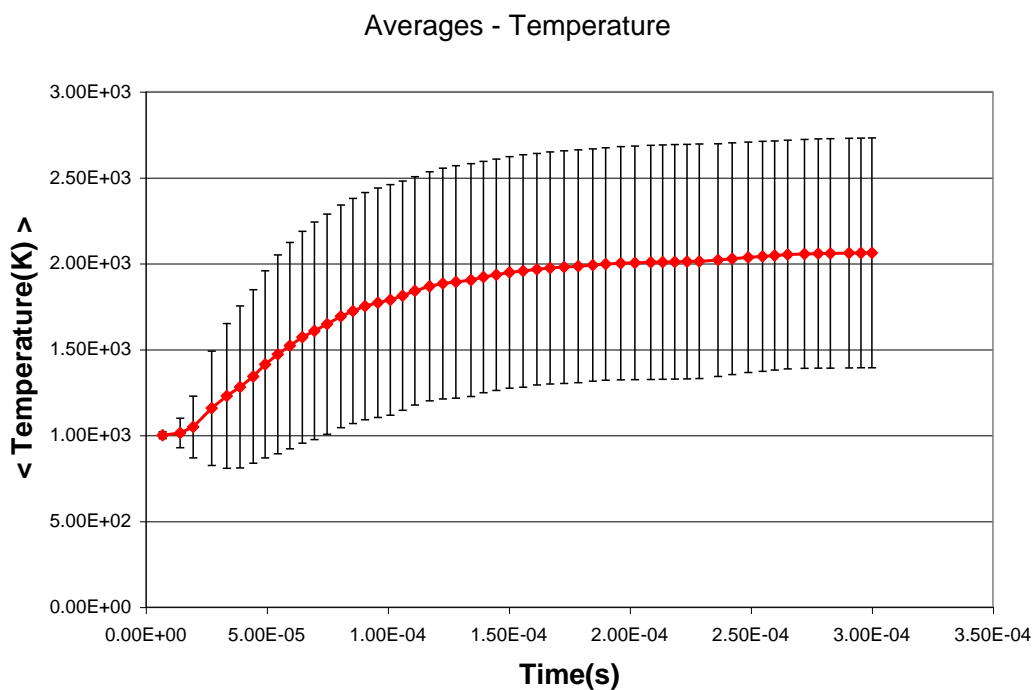


Figure 21. Average temperature profiles from the H₂-O₂ combustion run under constant pressure with error bars from 100 sample runs with “-CONF” switch. Again, these average results are vastly different from the single run shown in figure 18 above!

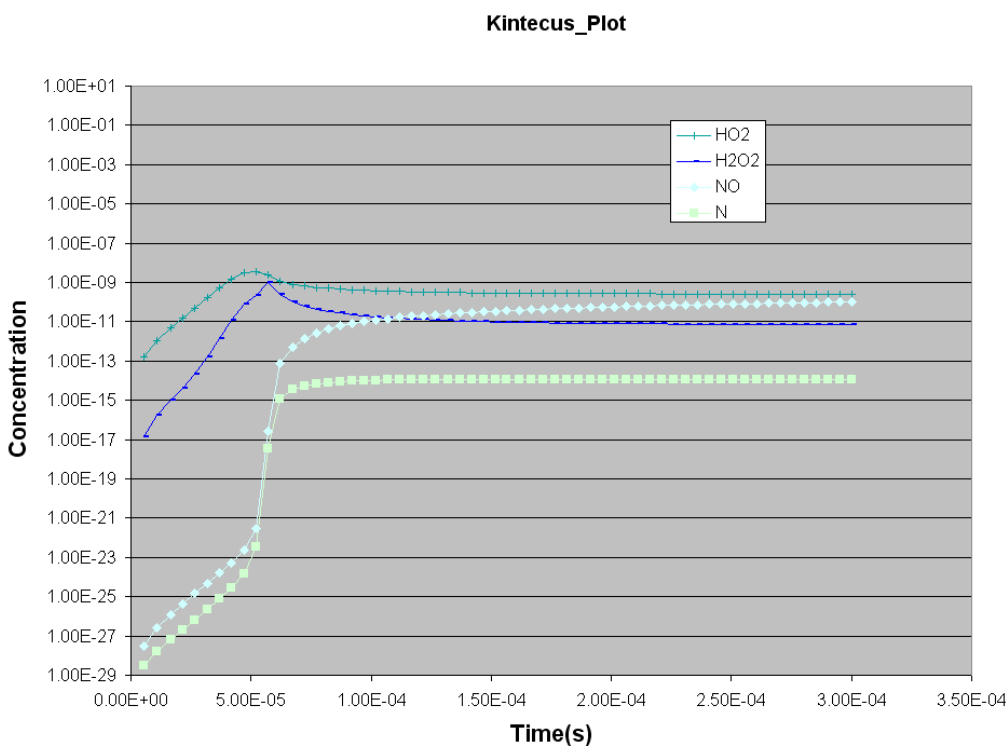


Figure 22. A single run showing the time profile for HO_2 , H_2O_2 , NO and N .

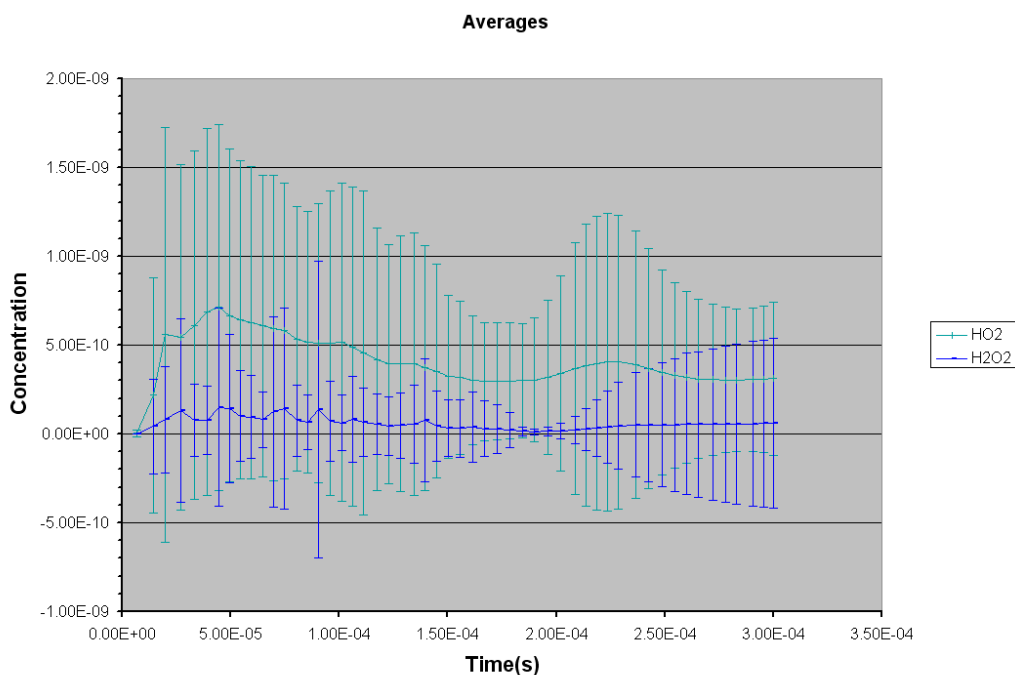


Figure 23. Plot of the HO_2 and H_2O_2 average concentrations with error bars of one-sigma for the uncertainty run of the $\text{H}_2\text{-O}_2$ combustion under adiabatic conditions, constant pressure. These average concentrations are close to the concentrations in figure 21 that were generated from single-run using nominal initial conditions, but there is great intermediate variations in the concentration time profiles.

8. Scanning

Background

The ability to scan (also known as sweeping or parametric study) important 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 turn on through inclusion of the “-scan” switch.

Implementation

Kintecus V3.8 allows one to easily perform such scans in four different ways: sequential, parallel with no repeat, parallel with repeating and combinatorial. Each of those scanning implementations are discussed below. Scanning in Kintecus is turn on through inclusion of the “-scan” switch.

Parameters that are to be scanned are setup 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 1×10^5 to 1×10^6 in increments of 1×10^5 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 are using the current V3.8 Kintecus-Excel spreadsheets then Kintecus will automatically plot all your scans onto on graph. Each species name/temperature will be suffixed with the concnnnnn.txt file its associated with. 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)?
- 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 a total number of 37 scans will be performed creating 37 conc#####.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 to 1000 followed by the initial concentration from 0 M to 2 M then 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 given above only 20 total scan conc#####.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, in this case 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 exact manner as the above mentioned **Parallel Scan No Repeat**, but once a scanned value reaches its final value, it then starts all over again, thereby repeating until the slowest changing parameter reaches its final scan value.

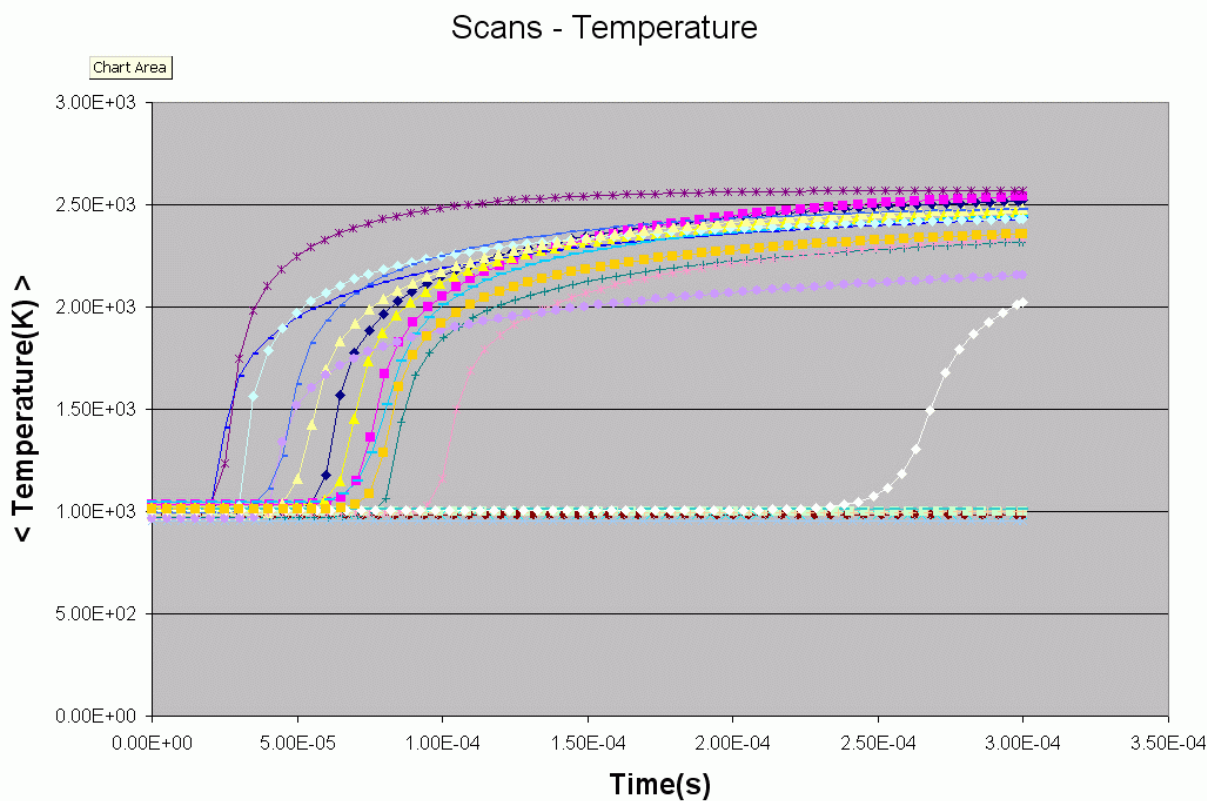
Combinatorial Scan

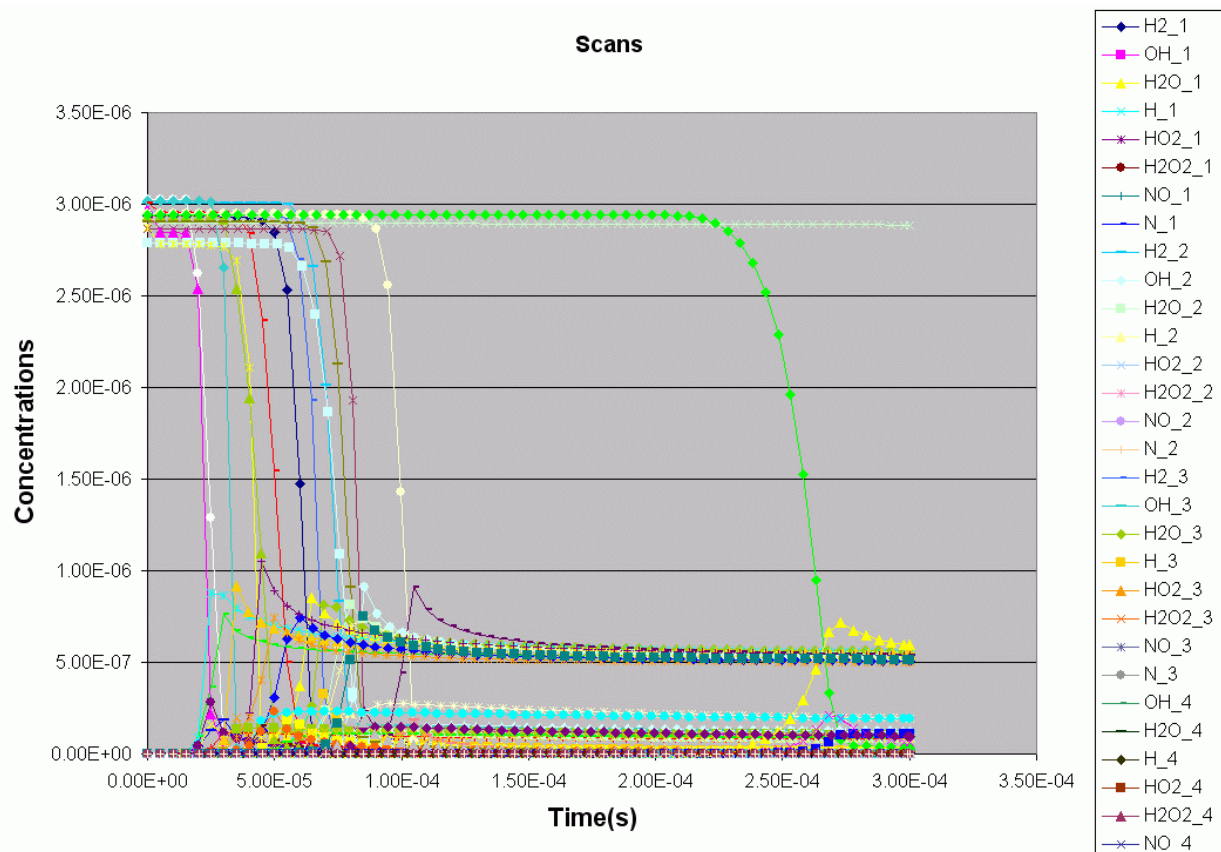
This type of scan will produce all the possible combinations between all the scanning values. Consequently this type of scan can produce extremely large amounts of data. For the scan example above, invoking a combinatorial

scan (-scan:4) will produce 1,320 concnnnn.txt files!!! If you are using the Kintecus-Excel spreadsheet and you are performing combinatorial scans, it is highly recommended that you only display the species you are interesting 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 very simple scanning example scans the starting concentration of O2 creating a several different runs. Interesting, there is a very long ignition delay for one run. This run has an ignition delay that is over an order of magnitude (1,000% !!!) longer than the other runs!





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 has the ability to group related and unrelated parts of temporal concentration profiles in a meaningful, quantitative way. This grouping allows a user to clearly see patterns that were initially indiscernible or hidden.

"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 positively, zero or negatively correlated to each other and with other groups/species in either a pictorially or numeric output or both. This 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 with 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 H₂, O₂ 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 pictorially 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 fully examined...

Cluster analysis becomes quite a powerful tool when coupled with combinatorial scanning (see the [Scanning](#) Section to 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 all optional, but when setting options b to k all preceding options must be specified. 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 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 to 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 between zero to eight (0-8) inclusively. The most common dissimilarity methods you will most likely use is the Euclidean distance (set option “b” to zero, “0”) and other the 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]	$\text{Sqrt}(\text{Sum}(\text{distance between } [c_1]_i \text{ and } [c_2]_i^2))$	Euclidean distance between concentration profiles
1	$\text{Sum}(\text{ABS}(\text{distance between } [c_1]_i \text{ and } [c_2]_i))$	Norm of L1 of concentration profiles
2	$\text{Max}(\text{distance between } [c_1]_i \text{ and } [c_2]_i)$	Norm of L-at-infinite
3	Mahalanobis distance	Mahalanobis distance
4	$\text{Cos}(\text{theta between vectors } [c_1]_i \text{ and } [c_2]_i)$	Dot product between concentration profiles
5	Just theta between vectors $[c_1]_i$ and $[c_2]_i$	Angle
6	Rho from a plot of $[c_1]_i$ and $[c_2]_i$	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 $[c_1]_i$ match $[c_2]_i$	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” has no affect on 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]	Minimum distance between cluster (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 really used that often)
2	Convert the values in the similarity/dissimilarity matrix into distances by obtaining the reciprocal of the absolute value: $1/ \text{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 the calculation of 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 concentration temporal 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 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 as the **most useful**:

“-cluster:1:6:0:2”

which implements the very useful 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 very useful correlation technique was not set as the default because occasionally it fails due to some species’ temporal concentration profiles have no change and are near zero. This 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 (or 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 is 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:

```
+++++
EIS*****
      *
      8*****
      *
EI*****
      *
      10*****
      *      *
ES*****
      *      *      *
      9*****
      *      *
E*****
      *      *
      11*****
      *      *
I*****
      *      *
      12*****
      *      *
P*****
      *      *
      13*****
      *
S*****
+++++
```

We can see that enzymes EIS and EI and ES and E are both in their own 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 indeed EIS, EI are quite close together and all by themselves. Species E and ES show a similar pattern hence their own little cluster. Species I, P and S are in their own branches alone, but species I is closer to the EIS, EI and ES, E clusters than P or S.

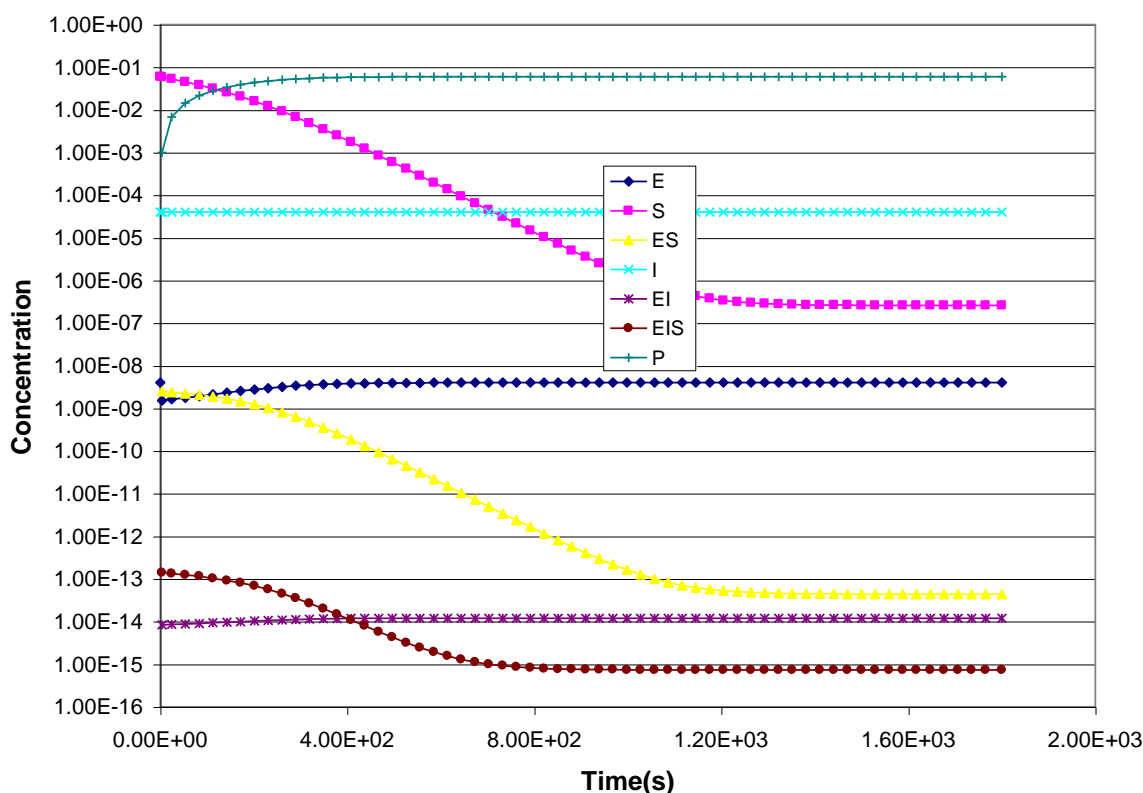


Figure 24. Temporal Concentrations plot of the Sample Enzyme Model. (y-axis is on a logarithmic scale)

Cluster Analysis: Sample 2

Lets see a more useful 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 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"** . There is **one small problem with this distance measure**, since the concentration of species "I" never changes, the r^2 's with plotting species "I" will always be zero. This 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:

```

+++++
EIS*****
      *
      7*****
      *
ES*****
      *
      *
      8*****
      *
EI*****
      *
      *
      9*****
      *
P*****
      *
      *
      *
      11*****
      *
S*****
      *
      *
      10*****
      *
E*****
+++++

```

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 that appear 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 as they have 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 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 ($r^2=0.296$).

Let's try another Hierarchical Cluster analysis utilizing correlation distances for the similarity matrix and a minimum grouping between clusters on the O₂ and H₂ 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, while 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 on 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 there are three main families of clusters 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*****
      *

```

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

			*	*	*	*	*	*
			79*	*	*	*	*	*
			*	*	*	*	*	*
ch2co*	*****			*	*	*	*	*
			*	*	*	*	*	*
			87*	*	*	*	*	*
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*****		*	*	*	*	*	*	*

150

10. 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 and/or data and/or links can be entered in column I (column #9) onto the very 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 all those 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. You can view a sample video animation of the procedures below if you go to www.kintecus.org . 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) Okay, 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, 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 the rename the new worksheet to MODEL!

** 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 altogether. This 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, 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 permit 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 copy all your worksheets from your old to the the new ones. This 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,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" and automatically plot all related files.

11. FAQ

How do I ... ?

Plot more than 255 columns of data?

This is 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 the end of it.
- 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 now go 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 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 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 point your web browser to www.kintecus.org and look under the 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 than a simple $\text{time} = \text{distance} / \text{velocity}$ can be used, but if there is some turbulence than 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, you might also want to get the paper it references the model and experimental data from. 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 the CSTR at the same time?" and the answer is "YES". Kintecus allows different Residence Times in the CSTR for "special" instances of where zeolites, surfaces or other species inhibitor might slow the average flow of one species against another.

Specify a constant Pressure system ?

As 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 full registration forms. Education Institutions and/or Students can register here: <http://www.kintecus.com/academic.htm> .

Reference Kintecus ?

Ianni, James C., Kintecus, Windows Version 6.00, 2017, www.kintecus.com.

Of course, if you are using a non-Windows Version then specify the platform (Linux, SUN, etc.,)

There are some journals that 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 in 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 in the species description spreadsheet and enter in a non-reactive gaseous species such as Ar (Argon) or Nitrogen (N₂). The additional gaseous species does not have to be in any chemical reaction. Now, go in the "Initial Concentration" field and enter in a sufficiently high concentration to raise the pressure of the system. The ideal gas equation can be used as an approximation for the initial concentration [$\text{Concentration} = n/V = P/(R \cdot T)$]. 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.

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 capable of running the xls files.

The results from my Excel model DO NOT exactly match the Kintecus model run from the COMMAND line ?

Some users have notice 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 in 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 full number 3.14159265E+10 in the command line up 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 full 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 to first 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 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 parameters 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 this 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 quite sure your units are consistent, be sure to 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 will force Kintecus to integrate taking very small time steps. This will cause a significant delay to get 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 is an Excel only issue. If you don't use the Kintecus-Excel fitted plots then you can ignore this part.

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. 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 copy of the worksheet (right click on the worksheet tab, 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" to 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, then 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 are 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 you don't use graphical plots from Excel, then 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 really lousy and buggy Fortran Powerstation. It was released as shareware back in 1995. It is now 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, so hence the name. In 1995, Kintecus was moved from the Amiga to the DOS platform which only supports filenames of eight characters, so a letter will have to be hacked off the name. The letter, "E" was deleted and the "I" replaced to "E" so we get the current name "KINTECUS". The program was also Copyrighted in 1995 under "KINTECUS", so do to legal reasons that name has been kept.

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 seems to happen under Windows Vista/Windows 7. You probably have to install Kintecus into "C:\\" and NOT "C:\Program Files\" as for some reason, Vista/Windows 7 will not allow Kintecus to write files into "C:\Program Files\". This can also happen if you do not have write permission in the directory Kintecus is installed in. Kintecus writes various temporary files and output files into the directory it is installed in. You MUST have write permissions in the directory Kintecus is stored.

12. 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 then 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’s **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 than enter your reactions like so:

```
1.323e-4, A- + Widget-- + C==>G+++ + F---+H2O
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---+H2O
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 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 Time(s) heading on the same row. 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 just by adding the “**-conf**” switch on the command line. If you are in Excel, and you are using the latest Kintecus-Excel spreadsheets, then 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.

13. 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 in 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 that is 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 normally 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 in the initial concentrations for relevant reactants. If all the reactants have an initial concentration of zero then this will cause problems.*
- 2) *If you are sure you've done that than 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 1×10^{-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 1×10^{-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. $A \Rightarrow A$ is a meaningless reaction.*
- 5) *If your reaction scheme consists of thousands of reactions you could be experiencing large round-off error, try using the analytically calculated Jacobians by 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 this 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 NaN's 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 quite 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 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 to get to the final integration time.
- 8) If you are using the "-THERM" switch, ie, 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, starting concentration? Can you get new coefficient values that have a broader range for that species?

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 a space to delimit your data!

Fatal Error #2

'ERROR!, MORE THAN (number) COLUMNS OF DATA IN '
(filename)

Explanation:

You are using 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 a space to delimit your data! Spaces are ignored by Kintecus 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 are using either a TABS, commas, colons and '|' as a data delimiter. You can not use a space as a data delimiter. Spaces are ignored by Kintecus 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 are using either a TABS, commas, semi-colons, colons and '|' as a data delimiter. You can not use a space as a data delimiter. All spaces are ignored by Kintecus. 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 can not 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 that must be provided when thermodynamics being 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 duplicate 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 a total of three unique reactants and three unique products in one reaction. This restriction DOES NOT include +M[...] or +S[...] appearing as a reactant, so the following reaction is allowed:



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 thermodynamic description
file:THERM.DAT

Explanation:

If you wish to use thermodynamics in your model, then you must provide thermodynamic coefficients for ALL species. If you are sure you did do this, then make sure that if you are using the Species Reservation field in the Thermodynamic Database Description Spreadsheet correctly. If you reserve a species for a database that does not contain the reserved species, you will get this error.

Fatal Error #76

To compute reverse rates using the thermodynamic
database, please use UNITS of mol./liter, mol./cc or
molecules/cm³.

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? Remember, a '#' or a double quote as the very first non-space character on a line will comment the whole line out.

Warning Messages

Warnings will not halt a simulation run, but it may lead Kintecus to crashing, 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 [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.

14. 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. For the programs ending in .bas to run these, just type at the Command prompt >qbasic /run program.bas.

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. Make sure 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. Last step, copy the **parmck.dat** to **parm.dat** and the **THERMCK.DAT** to **THERM.DAT**. Make sure the thermodynamic database name in the first column matches the filename to the extracted Chemkin thermodynamic database. Note, not all Chemkin thermodynamic databases are a like, and you might have to try different ways of reading in the database. You can do this by simply uncommenting out the other lines in the THERM.DAT file. Naturally, be sure to comment out the line in the THERM.DAT that was not set correctly. 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 next 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 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 that are 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 to manually place in a semi-color between the species enhanced third body values and remove 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.

15. Trademarks

KINTECUS is a registered trademark of James C. Ianni. CHEMKIN and SENKIN are all trademarks or registered trademarks of Reaction Design or of Sandia National Laboratories.

All other product and company names are trademarks or registered trademarks of their respective companies or holders.

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17. Registration

Kintecus® Version 6 Registration

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Appendix A – Sample Statistical Output

```
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
```

```
Total optimization iteration count=      281
** Total amount of simulations performed=    918
```

The calculated stand. devs. and covariance matrix can be outputted by entering the **“-FITSTAT”** switch on the Kintecus command line.

```
Covariance Matrix:
  380726511738.027      84395658.4478283      -12399590966.1360
-0.955964597865071      226412.539349878      -37329936.5835151
-0.0293481851329124      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 * * *					
Source	DF	Sum of Squares	Mean Square	Overall F	Prob. of 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			

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 * * *
Source DF Sum of Mean Prob. of
Regression 1 0.009008 0.009008 ***** Larger F 0.0000
Residual 46 0.000000 0.000000
Corrected Total 47 0.009008

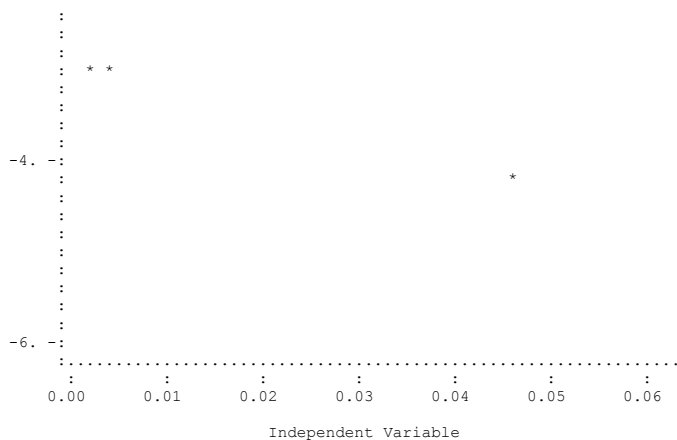
* * * Inference on Coefficients * * *
Coef. Estimate Standard Error t-statistic Prob. of Variance
Larger |t| Inflation
1 0. 7.638E-07 -1.6 0.1226 1.1
2 1. 5.316E-05 18814.8 0.0000 1.0

* * * Variance-Covariance Matrix for the Coefficient Estimates * * *
1 2
2 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
:



..

```

=====
***** 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)

```

**** 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 * * *
Source      DF      Sum of      Mean      Prob.
      Squares      Square      Overall F      Large
Regression      1      7.177E-26      7.177E-26      *****      0.0
Residual      30      2.840E-31      9.465E-33
Corrected Total      31      7.177E-26

      * * * Inference on Coefficients * * *
Coef.      Estimate      Standard      t-statistic      Prob. of      Variance
      Error      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
=====

```

