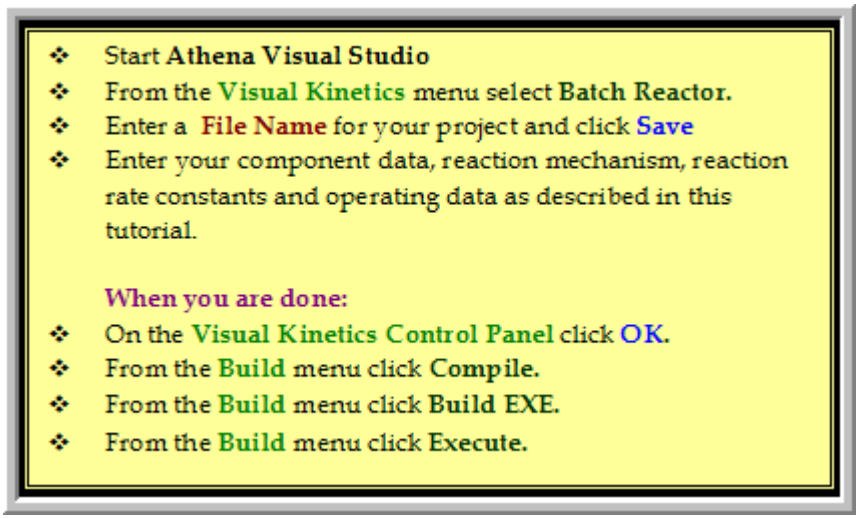
Athena Visual Studio Visual Kinetics Tutorial

VisualKinetics™ is an integrated tool within the Athena Visual Studio software environment, which allows scientists and engineers to simulate the dynamic behavior of homogeneous and heterogeneous chemical reactions. Chemical reactions may include but not limited to, microbial growth kinetics, pharmacokinetics, food preparation kinetics, enzymatic reactions, and combustion reactions and many more. In addition **VisualKinetics™** allows the user to perform sensitivity analysis and compare simulation results with experimental data in order to estimate unknown parameters. Rigorous statistical methods based on Bayes' theorem and implemented in **VisualKinetics™** allow for model criticism and lack-of-fit analysis, rival model discrimination as well as optimal experimental design. More specifically, the following tasks are implemented in **VisualKinetics™**



Modeling of Complex Reaction Networks: Allows the user to design and build reaction network, by entering species, reactions, kinetic and adsorption parameters and miscellaneous other operating conditions either via a graphical user interface or a text file. Athena compiles the user information and creates a subroutine named by the user; this subroutine is written in FORTRAN 95 and it is callable form compatible environments.

Reactor Modeling: Allows the user to design and build reactor models, by entering species, reactions, kinetic and adsorption parameters and miscellaneous other operating conditions either via a graphical user interface or a text file. The reactor models available through the interface are Batch, Semi-Batch, and Continuous Stirred Tank Reactors, Plug Flow and Fixed Bed Reactors. The reactor models can be isothermal, adiabatic or non-isothermal.

Simulation: Once the kinetic model is implemented and the proper data entered, **VisualKinetics™** generates the required interface to the Athena Visual Studio computational engines in order to perform various simulation studies and investigate the dynamic and steady state behavior of the chemical species. In this mode the user can exploit the rich environment of Athena Visual Studio and perform sensitivity analysis and parametric continuation studies.

Statistical Analysis and Nonlinear Parameter Estimation: This unique feature of **VisualKinetics™** permits the user to set up parameter estimation problems via the graphical interface. In this setup the user brings the experimental data, and easily selects the model responses and parameters that need to be estimated. **VisualKinetics™** then creates the proper interface to Athena Visual Studio's statistical analysis engines, such as weighted Least Squares and Bayesian Estimation techniques. A large number of tools are now available to the user, for statistical inferences on the model parameters, model discrimination and lack-of-fit as well optimal experimental design.

VisualKinetics™ Table of Contents

Tutorial: Benzene Oxidation Isothermal Batch Reactor

Reaction Mechanism and Reaction Rates:

The production of maleic anhydride by the oxidation of benzene in the presence of excess air is given by the following reaction mechanism:

Benzene Oxidation	$C_6H_6 + 4.5O_2 \xrightarrow{k_1} C_4H_2O_3 + 2CO_2 + 2H_2O$	$r_1 = \frac{k_1 C_{C_6H_6}}{1 + K_{C_6H_6} C_{C_6H_6}}$
Maleic Anhydride Cracking	$C_4H_2O_3 + 3O_2 \xrightarrow{k_1} 4CO_2 + 1H_2O$	$r_2 = \frac{k_2 C_{C_4H_2O_3}}{1 + K_{C_6H_6} C_{C_6H_6}}$
Benzene Cracking	$C_6H_6 + 7.5O_2 \xrightarrow{k_1} 6CO_2 + 3H_2O$	$r_3 = \frac{k_3 C_{C_6H_6}}{1 + K_{C_6H_6} C_{C_6H_6}}$

The values and description of the parameters for this process are given in the table below:

MODEL PARAMETERS	INITIAL CONDITIONS
$k_1 = 4280.0 \times \exp\left(-\frac{12660}{T}\right)$	$C_6H_6(0) = 10.0$
$k_2 = 70100.0 \times \exp\left(-\frac{15000}{T}\right)$	$C_4H_2O_3(0) = 0.0$
$k_3 = 26.0 \times \exp\left(-\frac{10800}{T}\right)$	$O_2(0) = 40.0$
$K_{C_6H_6} = 0.5$	$CO_2(0) = 0.0$
	$H_2O(0) = 0.0$

We wish to develop a reactor model called **VKBatchReactor** that would accept input by the user and perform a dynamic simulation of the process, yielding the species concentration profiles as a function of time.

This example tutorial is already precoded in Athena Visual Studio. If you do not wish to type the code on your own you may access it by doing the following:

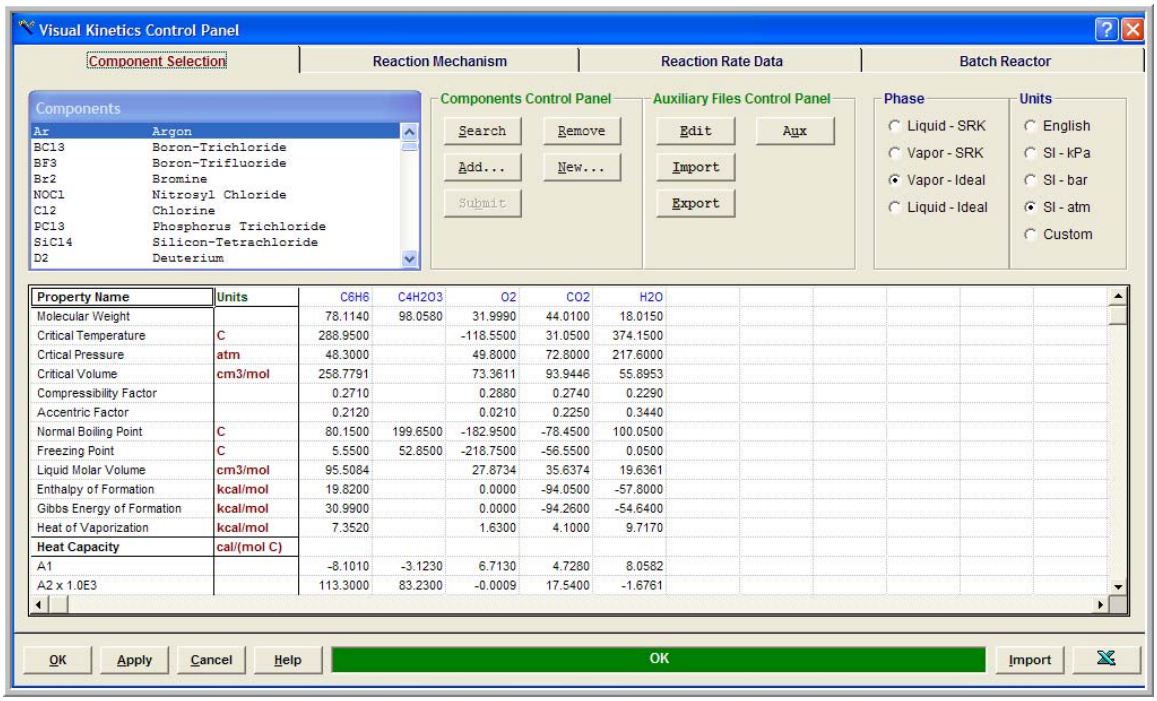
- Open **Athena Visual Studio**
- From the **File** menu click **Open**
- Navigate to **\Athena\Samples\Visual Kinetics** folder
- Select the **VKBatchReactor.avw** sample
- Click **OK**

Implementation in Athena Visual Studio

The following step by step process describes the model implementation in Athena Visual Studio

Component Selection

- Open **Athena Visual Studio**.
- From the **VisualKinetics** menu, choose **Batch Reactor**
- Enter a **File name** in the **New Model File** Dialog box and then Click **Save**.
- The *Visual Kinetics Control Panel* appears.
- You are now in the **Component Selection** tab.



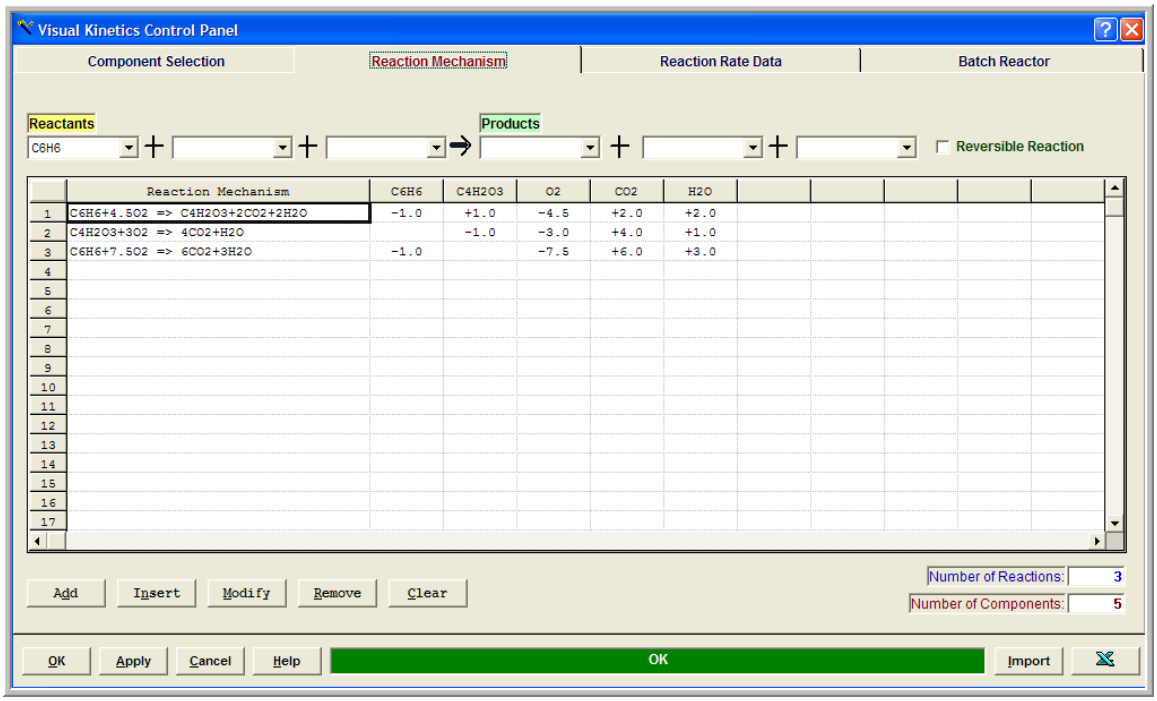
Ar	Argon
BCl3	Boron-Trichloride
BF3	Boron-Trifluoride
Br2	Bromine
NOCl	Nitrosyl Chloride
Cl2	Chlorine
PCl3	Phosphorus Trichloride
SiCl4	Silicon-Tetrachloride
D2	Deuterium

Property Name	Units	C6H6	C4H2O3	O2	CO2	H2O
Molecular Weight		78.1140	98.0580	31.9990	44.0100	18.0150
Critical Temperature	C	288.9500		-118.5500	31.0500	374.1500
Crtical Pressure	atm	48.3000		49.8000	72.8000	217.6000
Critical Volume	cm3/mol	258.7791		73.3611	93.9446	55.8953
Compressibility Factor		0.2710		0.2880	0.2740	0.2290
Accentric Factor		0.2120		0.0210	0.2250	0.3440
Normal Boiling Point	C	80.1500	199.6500	-182.9500	-78.4500	100.0500
Freezing Point	C	5.5500	52.8500	-218.7500	-56.5500	0.0500
Liquid Molar Volume	cm3/mol	95.5084		27.8734	35.6374	19.6361
Enthalpy of Formation	kcal/mol	19.8200		0.0000	-94.0500	-57.8000
Gibbs Energy of Formation	kcal/mol	30.9900		0.0000	-94.2600	-54.6400
Heat of Vaporization	kcal/mol	7.3520		1.6300	4.1000	9.7170
Heat Capacity	cal/(mol C)					
A1		-8.1010	-3.1230	6.7130	4.7280	8.0582
A2 x 1.0E3		113.3000	83.2300	-0.0009	17.5400	-1.6761

- **Search** for and **Add…** the reaction components [C_6H_6,$C_4H_2O_3$,O_2,CO_2,H_2O]. Click **New…** if you wish to add a user component that is not in the Athena Database.
- When you complete the selection of the reaction components click **Submit.** This action activates the Reaction Mechanism and Reaction Rate Data tabs. The Operating Data tab also is enabled in order to enter miscellaneous component properties and the reaction temperature and pressure.

Reaction Mechanism

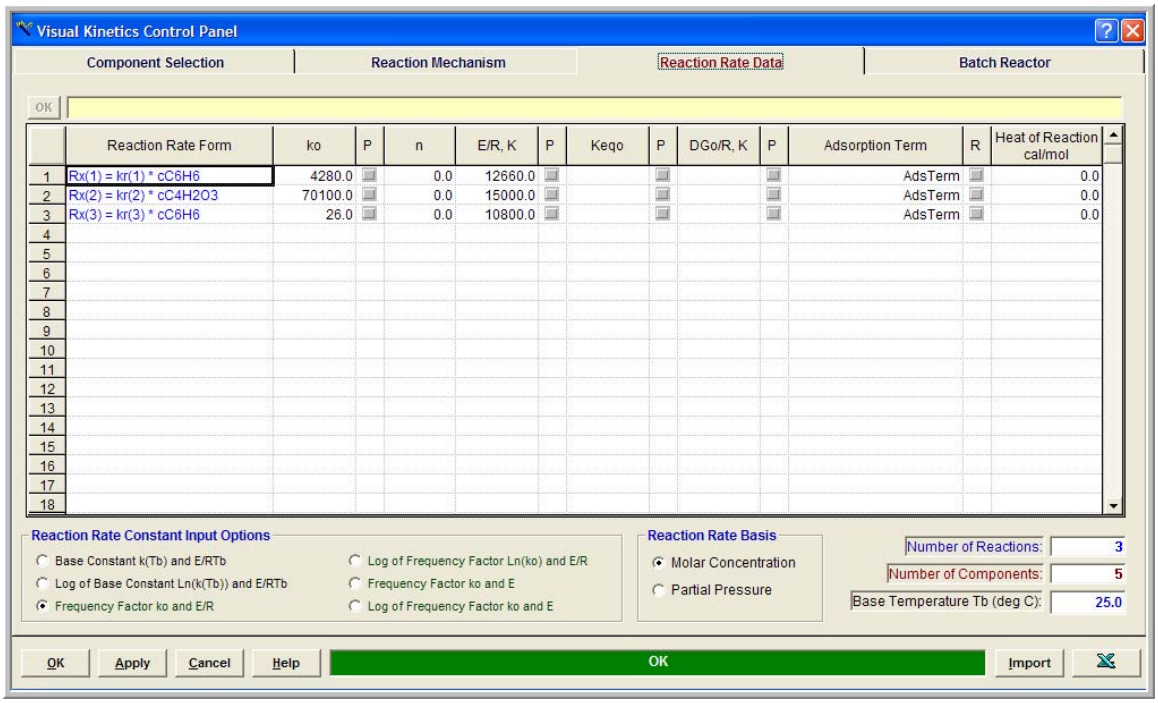
- Select the Reaction Mechanism tab.



- Formulate and **Add** the chemical reactions by selecting the Reactants and the Products from the drop down lists. Select blank from the drop down list if you wish to delete a component from a particular reaction. Use the **Insert**, **Modify** and **Remove** command buttons to edit your reaction scheme.
- Modify, if necessary, the stoichiometric coefficients (as indicated in this example). By default Athena assumes elementary reactions and therefore the stoichiometric coefficients can be the integers 1, 2 or 3. Should you wish to modify these coefficients to accommodate overall reaction mechanisms, such as cracking to miscellaneous components, you may do so by exporting your model into a data file, modifying the reaction rates and then re-importing the mechanism back into Athena.
- Use the **Clear** command button if something went wrong and you wish to start from the beginning.

Reaction Rate Data

❖ Select the **Reaction Rate Data** tab.



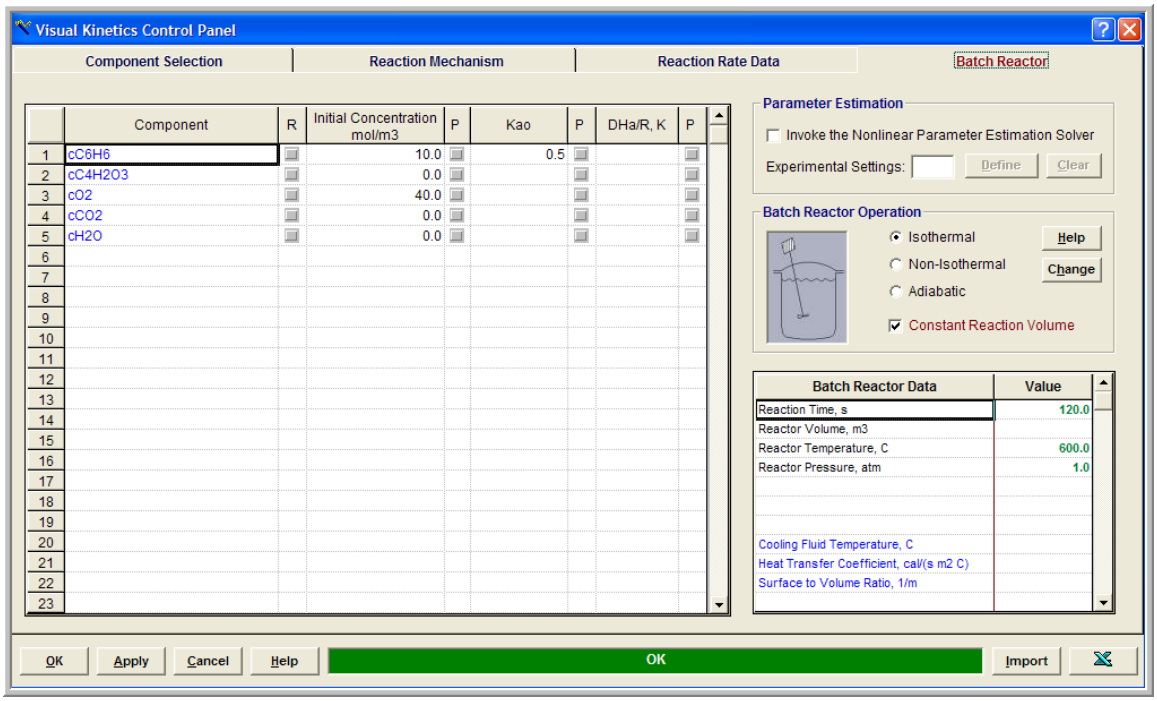
From the **Reaction Rate Constant Input Options** group, select the form of the reaction rate constants (in our example, *Frequency Factor and E/R*) and enter their numerical values. You may wish to enter values for the equilibrium constant if you have selected a reaction that is reversible; you may also wish to enter the adsorption terms for a heterogeneous reaction as indicated in this example. Recall that the general form of the reaction rate constants, equilibrium constants and species adsorption constants in Athena is given by the following equations:

$k = k_b \exp\left[n \ln\left(\frac{T}{T_b}\right) + \frac{E}{RT_b}\left(1 - \frac{T_b}{T}\right)\right]$	$k = k_0 T^n \exp\left[-\frac{E}{RT}\right]$
$K_{eq} = K_{eq,b} \exp\left[\frac{\Delta H_R}{RT_b}\left(1 - \frac{T_b}{T}\right)\right]$	$K_{eq} = K_{eq,0} \exp\left[-\frac{\Delta G}{RT}\right]$
$K_{ads} = K_{ads,b} \exp\left[-\frac{\Delta H_\alpha}{RT_b}\left(1 - \frac{T_b}{T}\right)\right]$	$K_{ads} = K_{ads,0} \exp\left[+\frac{\Delta H_\alpha}{RT}\right]$

Modify, if necessary, the reaction rate form by clicking on the reaction rate you wish to modify, entering the corrections in the yellow text box and then clicking **OK** to accept the rate changes.

Batch Reactor Data

- Select the **Batch Reactor** tab.



- Enter the Initial Concentrations of all chemical species of the reaction mixture.
- Enter, if necessary, the numerical values of the species adsorption constants.
- Enter the Reaction Time, Temperature and Reaction Pressure.
- Click **OK**

Simulate the Batch Reactor

You are now ready to save your Batch Reactor model and run it. In order to save your project:

- From the ***File*** menu, choose ***Save***. The *Save As* dialog box appears. This action saves your model and creates the Fortran code.
- In the Directories box, double-click a directory where you want to store the source file of your project.
- Type a filename (a filename cannot contain the following characters: \ / : * ? " < > |) in the File Name box, then choose **OK**. The default extension is **avw**
- To view the Fortran code that you created from the ***View*** menu choose ***Fortran Code***.

You may now choose to compile, build and execute your project; to do that:

- From the ***Build*** menu choose ***Compile*** (or **Hit F2**)
- From the ***Build*** menu choose ***Build EXE*** (or **Hit F4**)
- From the ***Build*** menu choose ***Execute*** (or **Hit F5**)

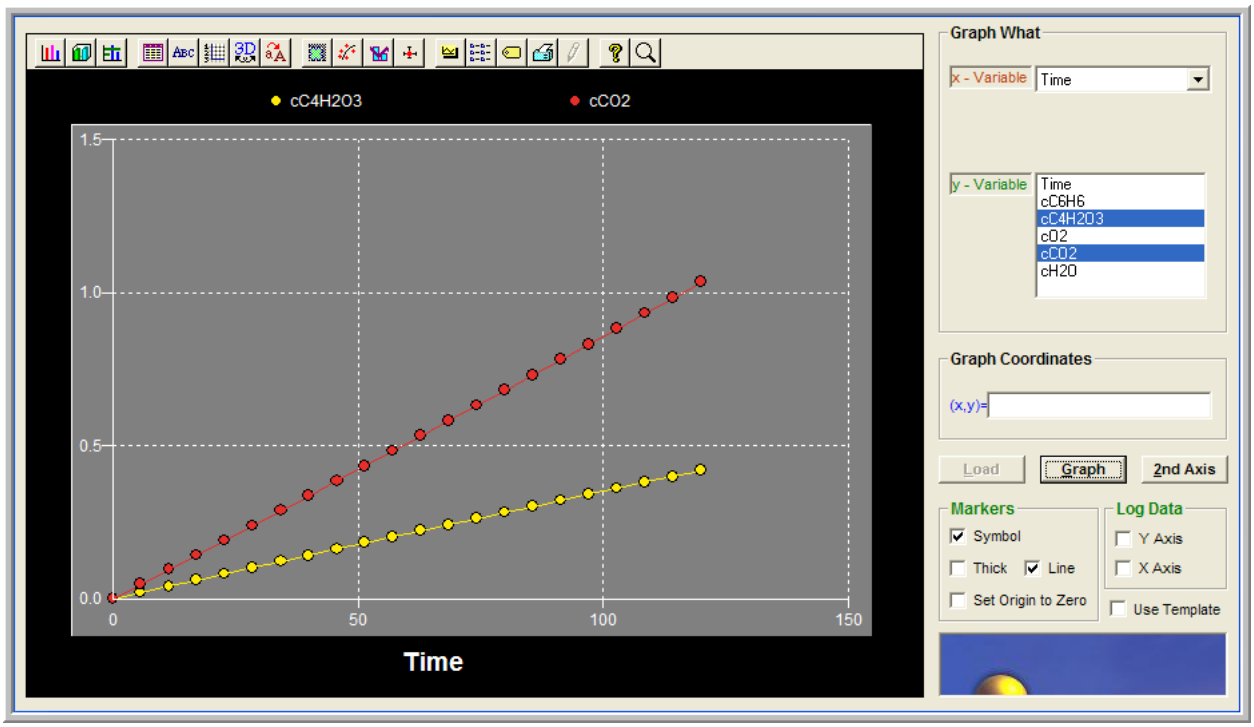
Numerical Results

If everything goes well the results window will appear. In this window you can see the solution of your problem as well as various statistics pertaining to the solution process:

```
Number of State Equations.....................     5
Number of Sensitivity Parameters..............     0
Number of Integration Output Points...........    22

 TIME          U(1)          U(2)          U(3)          U(4)          U(5)
 0.00000E+00   1.00000E+01   0.00000E+00   4.00000E+01   0.00000E+00   0.00000E+00
 5.71429E+00   9.97838E+00   2.05459E-02   3.98995E+01   4.75484E-02   4.43201E-02
 1.14286E+01   9.95676E+00   4.10375E-02   3.97988E+01   9.52679E-02   8.86714E-02
 1.71429E+01   9.93516E+00   6.14739E-02   3.96981E+01   1.43161E-01   1.33054E-01
 2.28571E+01   9.91356E+00   8.18552E-02   3.95973E+01   1.91227E-01   1.77469E-01
 2.85714E+01   9.89197E+00   1.02181E-01   3.94963E+01   2.39467E-01   2.21915E-01
 3.42857E+01   9.87039E+00   1.22452E-01   3.93952E+01   2.87880E-01   2.66392E-01
 4.00000E+01   9.84881E+00   1.42667E-01   3.92941E+01   3.36468E-01   3.10901E-01
 4.57143E+01   9.82724E+00   1.62827E-01   3.91928E+01   3.85229E-01   3.55442E-01
 5.14286E+01   9.80568E+00   1.82932E-01   3.90914E+01   4.34164E-01   4.00014E-01
 5.71429E+01   9.78413E+00   2.02980E-01   3.89899E+01   4.83273E-01   4.44617E-01
 6.28571E+01   9.76259E+00   2.22974E-01   3.88884E+01   5.32557E-01   4.89252E-01
 6.85714E+01   9.74106E+00   2.42911E-01   3.87867E+01   5.82015E-01   5.33918E-01
 7.42857E+01   9.71953E+00   2.62793E-01   3.86849E+01   6.31647E-01   5.78616E-01
 8.00000E+01   9.69801E+00   2.82618E-01   3.85829E+01   6.81454E-01   6.23346E-01
 8.57143E+01   9.67650E+00   3.02388E-01   3.84809E+01   7.31436E-01   6.68106E-01
 9.14286E+01   9.65500E+00   3.22102E-01   3.83788E+01   7.81592E-01   7.12899E-01
 9.71429E+01   9.63351E+00   3.41760E-01   3.82766E+01   8.31924E-01   7.57722E-01
 1.02857E+02   9.61202E+00   3.61362E-01   3.81742E+01   8.82430E-01   8.02577E-01
 1.08571E+02   9.59054E+00   3.80908E-01   3.80718E+01   9.33112E-01   8.47464E-01
 1.14286E+02   9.56907E+00   4.00397E-01   3.79692E+01   9.83969E-01   8.92381E-01
 1.20000E+02   9.54761E+00   4.19830E-01   3.78666E+01   1.03500E+00   9.37331E-01

EXIT DDAPLUS: SOLUTION FOUND

Number of Steps Taken Thus Far..................      18
Number of Function Evaluations..................      72
Number of Jacobian Evaluations..................       6
Number of Jacobian Factorizations...............       6
```

Graphical Results

If you wish to see the time profiles for all the species that participate in this fermentation process from the ***View*** menu choose ***Solution Graphs***. The Athena Visual Studio graphics control panel appears:



In this window fist we click ***Load*** to load the numerical results. Then in the **Graph What** group we select the **x-variable** (here **Time**) and the **y-variable** (here two of the state variables by holding the **Ctrl** key down and clicking with your mouse on the two variables) and click ***Graph***. You should see the graph that appears above. You may now click on the graph toolbar and modify the type, title, symbol, the style and miscellaneous other properties of the graph.