

Athena Visual Studio Parameter Estimation Tutorial

- ❖ Start **Athena Visual Studio**
- ❖ From the **File** menu select **New**.
- ❖ You are in the **Process Modeling** tab.
- ❖ Select the **Parameter Estimation** tab.
- ❖ Click **Estimation with Ordinary Differential Equations**.
- ❖ Select **A Blank Document** and click **OK**.
- ❖ Enter your model data, initial conditions and equations, and the Athena solver data and options as described in this tutorial.

When you are done:

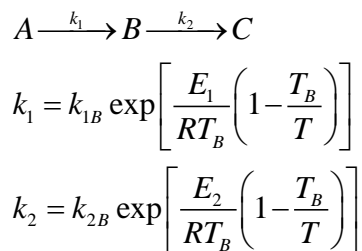
- ❖ From the **File** menu click **Save**.
- ❖ Navigate to the folder where you wish to save and enter a proper filename for your model.
- ❖ From the **Build** menu click **Compile**.
- ❖ From the **Build** menu click **Build EXE**.
- ❖ From the **Build** menu click **Execute**.

Nonlinear Model Parameter Estimation with implicit or explicit models may include nonlinear systems of algebraic equations, mixed systems of differential and algebraic equations, as well as boundary value problems or partial differential equations. This example problem has been created to test the functionality of Athena Visual Studio in dealing with the nonlinear parameter estimation of reaction rate constants from multi-response data at different temperature levels

with systems of ordinary differential equations. Experimental data at different temperature levels allows to estimate both the reaction activation energy and the reaction rate constant at a base temperature.

Tutorial: Nonisothermal Batch Reactor Kinetics Parameter Estimation

Reaction Mechanism and Reaction Rate Constants:



Reaction Rate Model:

The following model has been postulated as plausible candidate to describe the observed reactor concentration based on the available experimental data:

$$\frac{dC_A}{dt} = -k_1 C_A \quad \frac{dC_B}{dt} = -k_2 C_B + k_1 C_A$$

We wish to perform the following task:

- ❖ Estimate the parameters $\{k_{1B}, k_{2B}, E_1/RT_B, E_2/RT_B\}$ and their Highest Posterior Density Intervals [or Confidence Intervals].

The parameter initial guess at a base temperature T_B for this example is given in the table below:

MODEL INITIAL PARAMETERS	
$k_{1B} = 0.5$	$k_{2B} = 0.5$
$\frac{E_1}{RT_B} = 10.0$	$\frac{E_2}{RT_B} = 10.0$
$T_B = 25^{\circ}C$	

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\Parameter Estimation Models** folder
- ❖ Select the **PEM24.avw** sample
- ❖ Click **OK**

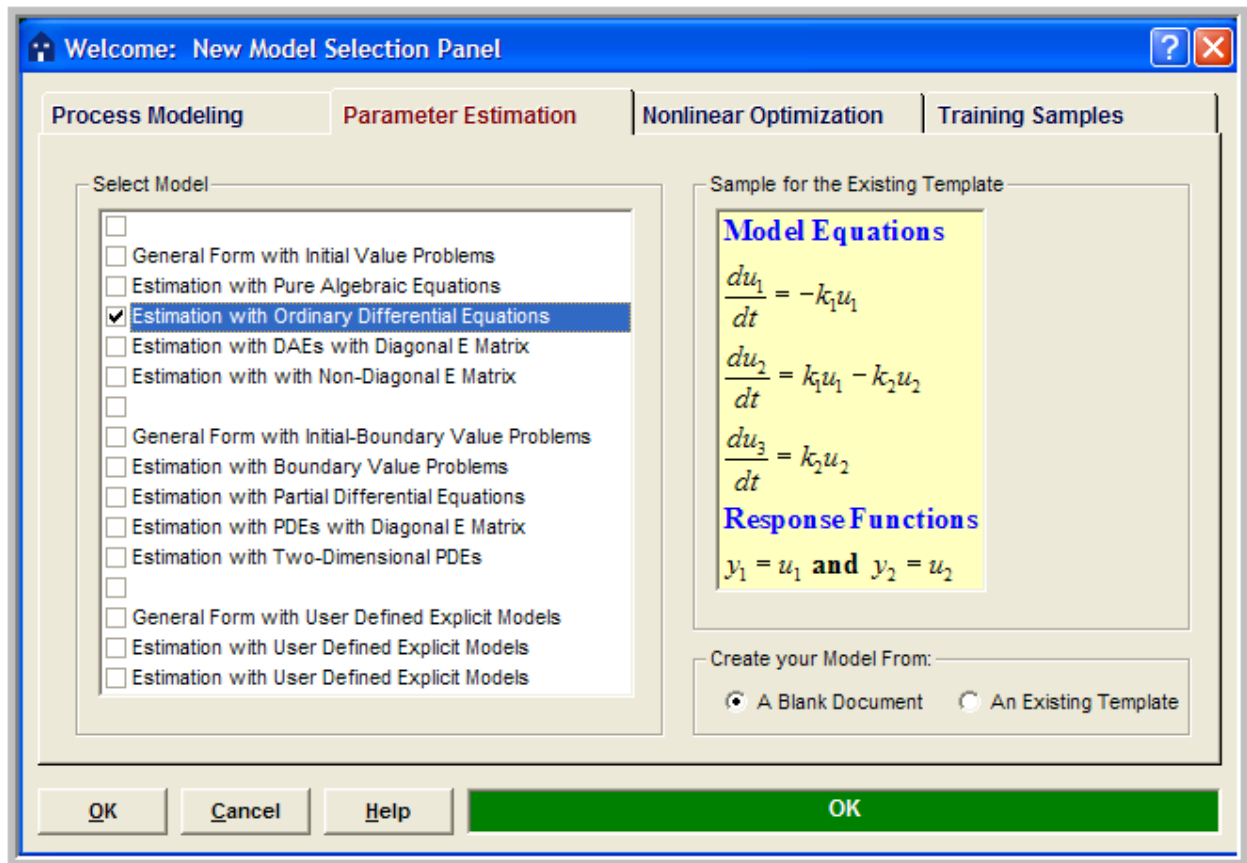
The experimental data at different levels of temperature and reaction time for this example are given below:

RunID	Time	Temp	Cao	Cbo	Ca	Cb
1	0.00	25.00	1.00	0.50	1.0000	0.5000
1	0.24	25.00	1.00	0.50	0.8669	0.7075
1	0.48	25.00	1.00	0.50	0.5590	0.6552
1	0.71	25.00	1.00	0.50	0.5385	0.8471
1	0.95	25.00	1.00	0.50	0.3472	0.7031
1	1.19	25.00	1.00	0.50	0.3345	0.8475
1	1.43	25.00	1.00	0.50	0.2157	0.6701
1	1.67	25.00	1.00	0.50	0.2078	0.7796
1	1.90	25.00	1.00	0.50	0.1340	0.6002
1	2.14	25.00	1.00	0.50	0.1291	0.6838
1	2.38	25.00	1.00	0.50	0.0832	0.5177
1	2.62	25.00	1.00	0.50	0.0802	0.5820
1	2.86	25.00	1.00	0.50	0.0517	0.4358
1	3.10	25.00	1.00	0.50	0.0498	0.4855
1	3.33	25.00	1.00	0.50	0.0321	0.3608
1	3.57	25.00	1.00	0.50	0.0309	0.3993
1	3.81	25.00	1.00	0.50	0.0199	0.2950
1	4.05	25.00	1.00	0.50	0.0192	0.3250
1	4.29	25.00	1.00	0.50	0.0124	0.2392
1	4.52	25.00	1.00	0.50	0.0119	0.2626
1	4.76	25.00	1.00	0.50	0.0077	0.1927
1	5.00	25.00	1.00	0.50	0.0074	0.2109
2	0.00	35.00	0.95	0.53	0.9500	0.5300
2	0.24	35.00	0.95	0.53	0.7467	0.7905
2	0.48	35.00	0.95	0.53	0.4147	0.7285
2	0.71	35.00	0.95	0.53	0.3441	0.9045
2	0.95	35.00	0.95	0.53	0.1911	0.7106
2	1.19	35.00	0.95	0.53	0.1586	0.8055
2	1.43	35.00	0.95	0.53	0.0881	0.5972
2	1.67	35.00	0.95	0.53	0.0731	0.6507
2	1.90	35.00	0.95	0.53	0.0406	0.4692
2	2.14	35.00	0.95	0.53	0.0337	0.5010
2	2.38	35.00	0.95	0.53	0.0187	0.3558
2	2.62	35.00	0.95	0.53	0.0155	0.3755
2	2.86	35.00	0.95	0.53	0.0086	0.2643
2	3.10	35.00	0.95	0.53	0.0071	0.2771
2	3.33	35.00	0.95	0.53	0.0040	0.1940
3	0.00	45.00	1.03	0.47	1.0300	0.4700
3	0.24	45.00	1.03	0.47	0.5969	0.8858
3	0.48	45.00	1.03	0.47	0.2650	0.7777
3	0.71	45.00	1.03	0.47	0.1758	0.8916
3	0.95	45.00	1.03	0.47	0.0780	0.6418
3	1.19	45.00	1.03	0.47	0.0518	0.6662
3	1.43	45.00	1.03	0.47	0.0230	0.4532
3	1.67	45.00	1.03	0.47	0.0152	0.4545
3	1.90	45.00	1.03	0.47	0.0068	0.3025
3	2.14	45.00	1.03	0.47	0.0045	0.2991
3	2.38	45.00	1.03	0.47	0.0020	0.1972

Implementation in Athena Visual Studio

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

- ❖ Open **Athena Visual Studio**.
- ❖ From the **File** menu, choose **New**.
- ❖ The *Welcome: New Model Selection Panel* window appears.



- ❖ Select the *Parameter Estimation* tab
- ❖ Select the *Estimation with Ordinary Differential Equations* option.
- ❖ Choose *A Blank Document* and click **OK**.

Type your source code in the new window. The source code contains standard modeling sections (see description in the next sections below); it may also contain calls to the available math and engineering procedures as well as user-defined procedures.

Writing the Source Code

You must enter a minimum of four sections in order to create the parameter estimation model with a system of differential equations. The first section labeled **@Initial Conditions** is used to insert initial values for the state variables vector. The second section labeled **@Model Equations** is used to enter the implicit model equations. The third required section labeled **@Response Model** is used to define the experimental responses(observations). The vector **Y(i)** is reserved in Athena to define these responses A section labeled **@Gradient Vector** is optional and may be used to enter the derivatives of the responses with respect to the adjustable parameters. The matrix **dY(i,k)** is reserved in Athena to define these derivatives . The fourth and final section labeled **@Connect Parameters** is used to connect the adjustable parameters and settings with the differential model parameters and constants. A data section not labeled by Athena Visual Studio may also be used to enter all the data pertinent to the model. The data section may also contain declaration statements for all model variables, parameters and constants. This section, if used, must be the first one in the model. The declaration of the model variables, parameters and constants must be done in accordance the Athena Visual Studio syntax rules shown below:

Data Section

In the data section the user simply enters the problem data and various constants. The data section also contains the declarations of problem variables, parameters and constants. For our example the user enters the experimental base temperature and the universal gas constant as shown in the code below. The Athena interpreter treats any line that begins with an exclamation mark **!** as a comment. It is mandatory and strongly recommended that the users declare all the problem parameters and constants. All variables in Athena are either real double or single precision or integer long. Character and Logical variables are also allowed. The following source code may be entered for this example (If you use the Windows Copy and Paste commands to enter this code into your Athena Visual Studio project, please beware that invisible format symbols may also be copied and cause the compilation of your code to fail):

```
! Declarations and Model Constants
!-----
Global k1,k2,k1B,k2B,E1B,E2B As Real
Global Tb,Temp,RxnTime,Rg As Real

Tb=32.5+273.15      ! Base Temperature, deg K
Rg=8.314           ! Universal Gas Constant, J/mol K
```

Declaration of Variables

Global Variables: To declare global variables in the Athena Visual Studio environment you must use the **Global** keyword as the examples below illustrate:

```
Global x, y, z, krate As Real  
Global Skount, Ncc As Integer  
Global myName As Character  
Global myDecision As Logical
```

In the above statements the variables *x, y, z, krate* will be treated as double precision and will be accessible by all modeling sections. Similarly the variables *Skount, Ncc* will be treated as integer and be accessible by all modeling sections. Character variables are assigned as Character*132 from the Athena Visual Studio parser. Single precision variables cannot be declared **Global**.

Vectors and matrices can be declared in a similar manner. The array size, type and number of dimensions are declared with the **Global** statement. The elements of the array can be referenced by an integer index number, which runs from one (or zero) to the maximum number declared in the **Global** statement:

```
Global y(10), c(0:5), a(4,50), b(2,4,6) As Real  
Global istate(5) As Integer
```

Local Variables: To declare local variables in the Athena Visual Studio environment you must use the **Dim** keyword as the examples below illustrate:

```
Dim Temp, Pres As Real  
Dim TotalFlow As Single  
Dim i As Integer
```

In the above statements the variables *Temp, Pres* will be treated as double precision, where as the variable *TotalFlow* will be treated as single precision; these variables will be accessible only at the section where they have been declared. Similarly the variable *i* will be treated as integer and will be accessible only by the corresponding modeling section where it has been declared.

Vectors and matrices can be declared in a similar manner. The array size, type and number of dimensions are declared with the **Dim** statement. The elements of the array are referenced by an integer index, which runs from one(or zero) to the number declared in the **Dim** statement:

```
Dim c(10), p(4,50) As Real  
Dim streamEnthalpy(10) As Single  
Dim irrow(5) As Integer
```

Parameter Statement: Use the **Parameter** keyword to define named constants as the examples below illustrate:

```
Parameter y=2.0, z=4.0 As Real  
Parameter Skount=1, Ncc=4 As Integer
```

In the above statements the variables *y*, *z* will be treated as double precision and their numerical values will be accessible by all parts of the modeling code. Similarly the variables *Skount*, *Ncc* will be treated as integer and their numerical values will be accessible through out all the modeling sections. The **Parameter** keyword is only allowed in the data section of the Athena Visual Studio modeling code. If it is used in the other modeling sections it will be ignored. You may view the generated Fortran code to see how the parser interprets the **Parameter** keyword.

Important Note: Always remember to declare all of your variables. Athena treats **Real** variables as double precision, **Integer** variables as 4-byte integers, **Character** variables as Character*132 and **Logical** variables as **.True.** or **.False.** Single precision variables are only allowed if are declared as local with the **Dim** keyword.

Fortran 95 Declaration Statements: You can insert Fortran 95 declaration statements by prefixing them with the double dollar sign. Below please see a list of Fortran 95 declaration statements that you can insert in your Athena code. Consult your Fortran 95 manual for the syntax rules of variable and constant declarations:

```
$$Integer, Parameter:: dp=Kind(1.0D0)  
$$Integer, Parameter:: sp=Kind(1.0)  
$$Real(Kind=dp):: v1,v2  
$$Real(Kind=sp), Dimension(3):: a1,a2  
$$Integer:: I1, I2  
$$Character(Len=3):: s2,s3  
$$Character(Len=10), Dimension(2):: s1  
$$Logical:: Done  
$$Real(Kind=dp), Dimension(:), Allocatable:: w
```

We are now going to describe in detail the various steps involved in writing an implicit model for parameter estimation in the Athena Visual Studio environment. The modeling code is NOT case sensitive.

Initial Conditions

In the Initial Conditions section the user must enter the initial values for the unknown state vector. The initial values are required by the algorithm in DDAPLUS to start the integration. The user must do the selection of the unknown state variables. The user must also make sure that he/she has a well-defined system where the number of equations is equal to the number of unknowns. The unknown state vector is represented by the variable $\mathbf{U}()$ in Athena. For our example we choose $\mathbf{U}(1)$ to represent the concentration of A and $\mathbf{U}(2)$ to represent the concentration of B . To enter the heading for the Initial Conditions section for our example:

- ❖ From the *Model* menu choose *Initial Conditions* (or **Hit F11**)
- ❖ Enter the source code as shown below for our example.

```
@Initial Conditions
U(1)=Xu(4)
U(2)=Xu(5)
```

The vector $\mathbf{Xu}()$ is reserved by Athena Visual Studio to access the experimental settings. For our example $\mathbf{Xu}(1)$ is equal to the RunId, $\mathbf{Xu}(2)$ is equal to the reaction time, $\mathbf{Xu}(3)$ is equal to the reaction temperature, $\mathbf{Xu}(4)$ equal to the initial concentration of component A and $\mathbf{Xu}(5)$ equal to the initial concentration of the component B .

Model Equations

In the Model Equations section the user must enter the functions that describe the physical process. For example these functions may simply indicate the rate of change of the concentration of miscellaneous chemical components. The vector $\mathbf{F}()$ is reserved in the Athena environment to represent the values of these functions. For our example $\mathbf{F}(1)$ is used to represent the rate of change of the concentration of A and $\mathbf{F}(2)$ is used to represent the rate of change of the concentration of B . In this section the user may make use of temporary variables to calculate intermediate variables such as, for example, the reaction rates. This facilitates the model writing process and it is also a sign of good programming skills. To enter the Model Equations section for our example

- ❖ From the *Model* menu choose *Model Equations* (or **Hit F11**)
- ❖ Enter the source code as shown below for our example.

```
@Model Equations
F(1)=-k1*U(1)
F(2)= k1*U(1)-k2*U(2)
```


Response Model

In the Response Model section the user must enter the responses. The vector $\mathbf{Y}()$ is reserved to enter the responses. For example $\mathbf{Y}(1)$ represents the first measured response, $\mathbf{Y}(2)$ the second (if present) and so on. To enter the responses for your model:

- ❖ From the *Model* menu choose *Response Model* (or **Hit F11**)
- ❖ Enter the source code as shown below for our example.

```
@Response Model
```

```
Y(1)=U(1)
```

```
Y(2)=U(2)
```

Connect Parameters

In the Connect Parameters section the user must connect the adjustable parameters and experimental settings with the model parameters and constants. The vector $\mathbf{Par}()$ is reserved to access the adjustable parameters, and the vector $\mathbf{Xu}()$ is reserved to access the experimental settings. For example $\mathbf{Xu}(1)$ represents the first setting, $\mathbf{Xu}(2)$ the second if present and so on. To enter the Connect Parameters section for our model: [Notice how the reaction rate constants are calculated using the Arrhenius equation and how the temperature and reaction time are passed through to the Athena solver]

- ❖ From the *Model* menu choose *Connect Parameters* (or **Hit F11**)
- ❖ Enter the source code as shown below for our example.

```
@Connect Parameters
```

```
k1B=exp(Par(1))
```

```
E1B=Par(2)
```

```
k2B=exp(Par(3))
```

```
E2B=Par(4)
```

```
RxnTime=Xu(2)
```

```
Temp=Xu(3)+273.15
```

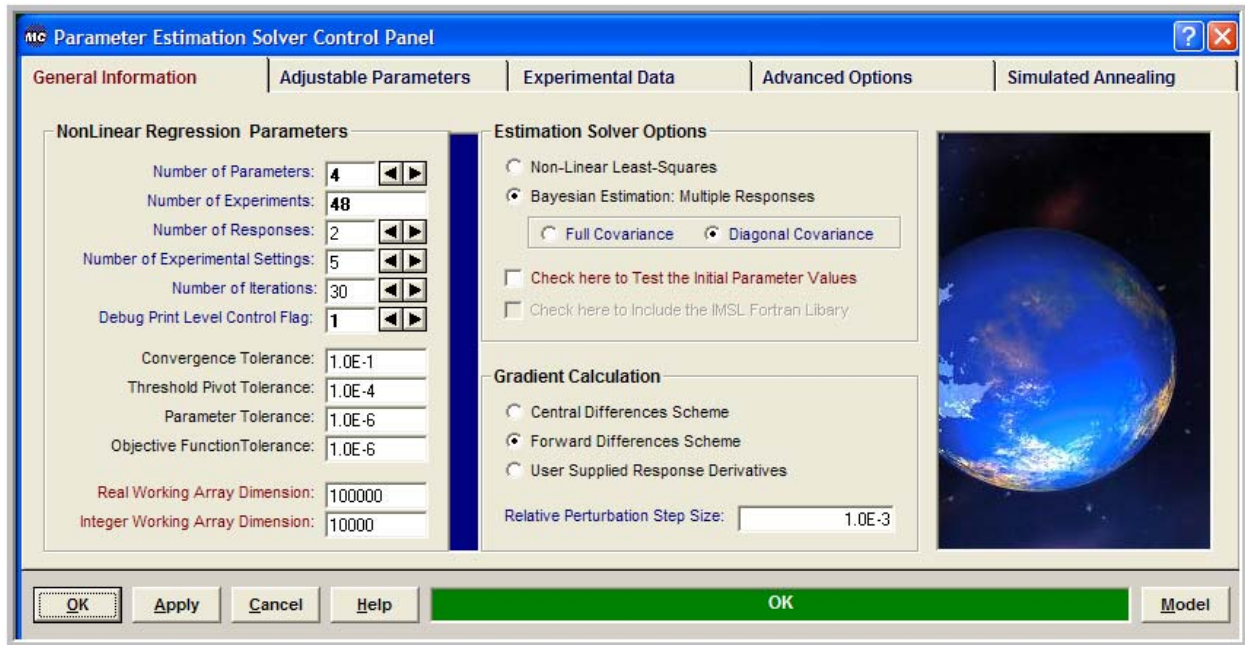
```
k1=k1B*exp(Par(2)*(1.0-Tb/Temp))
```

```
k2=k2B*exp(Par(4)*(1.0-Tb/Temp))
```

The Parameter Estimation Solver

It is now time to access the Athena Visual Studio solver for Parameter Estimation in order to enter information about the adjustable parameters, the experimental observations and various other parameters that control the estimation algorithm, To do that:

- ❖ From the *Model* menu choose *Load Solver* (or **Hit F12**)
- ❖ Enter the solver parameters as shown below for our example



From the **Nonlinear Regression Parameters** group enter:

- ❖ The number of parameters (4)
- ❖ The number of experiments (48)
- ❖ The number of responses (2) and
- ❖ The number of settings (5)

Optionally you may change the *Number of Iterations*, the *Convergence and Parameter Tolerance*, the *Debug Print Level Control Flag* and the *Real and Integer Working Arrays* space requirements. From the **Estimation Solver Options** group choose the type of estimation you are going to be using and optionally request a diagonal covariance if the Bayesian estimation has been chosen, or *Check here to Test the Initial Parameter Values*. The test call to model is a very useful option since it allows you to see how good is your initial parameter guess before you proceed with the estimation process. You also have the option to use a relative weighting factor of the observation vector in the estimation process. From the **Derivatives Calculation** group choose the method for the objective function gradient calculation and optionally enter the *Relative Perturbation Step Size*. Should you choose User Supplied Model Derivatives you must enter the section **@Gradient Vector** when you enter the source code.

The Adjustable Parameters

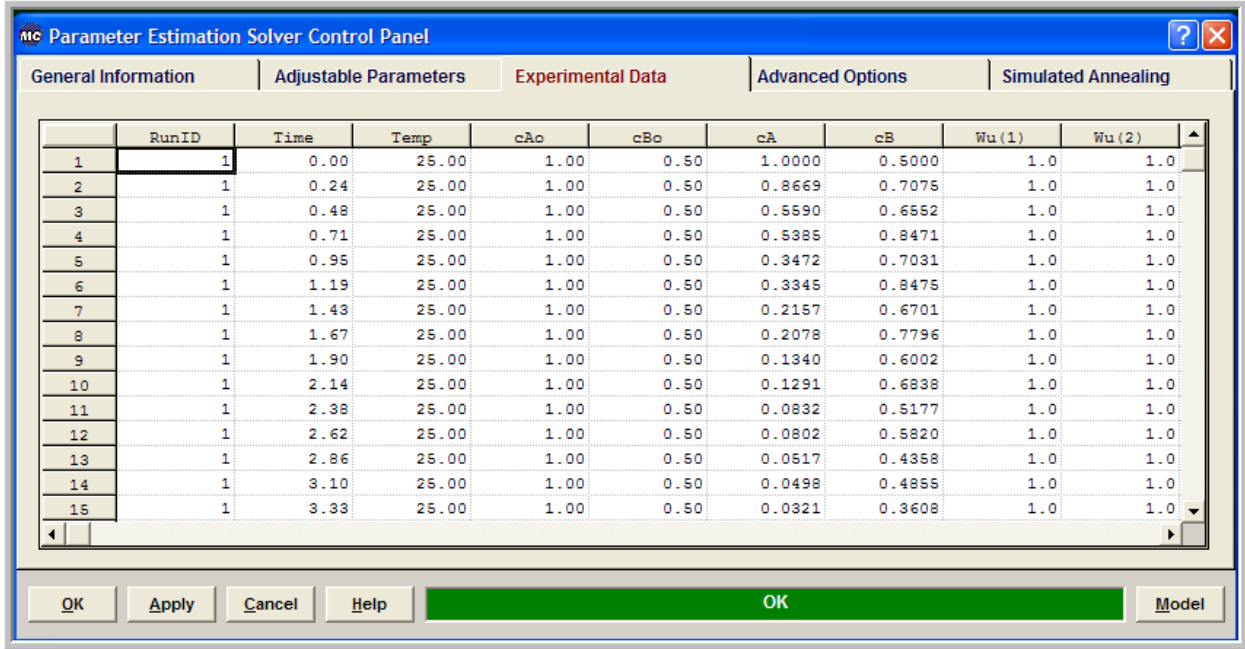
Next select the **Adjustable Parameters** tab on the Parameter Estimation Control Panel and enter the names of the parameters you wish to estimate, their initial guesses and optionally their lower and upper bounds, the relative perturbation step size for gradient computation and the size of the trust region. Notice that if a parameter is not checked in the check box next to it, will remain fixed at its initial value during the estimation. The following data have been inserted for our example:

	Names	<input type="checkbox"/>	Initial Value	Lower Bound	Upper Bound	Perturbation	Trust Region
1	Log (k1B)	<input checked="" type="checkbox"/>	0.5			-0.001	-0.75
2	E1B	<input checked="" type="checkbox"/>	10.0			-0.001	-0.75
3	Log (k2B)	<input checked="" type="checkbox"/>	0.5			-0.001	-0.75
4	E2B	<input checked="" type="checkbox"/>	10.0			-0.001	-0.75
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							

Buttons: OK, Apply, Cancel, Help, **OK**, Model

The Experimental Observations

Next select the **Experimental Observations** tab on the Parameter Estimation Control Panel and enter the observations and experimental settings. Optionally you may enter weights for each observation. Otherwise these weights are set equal to one by the Parameter Estimation solver. Windows Copy and Paste functions can be used to transfer your data from, say, an Excel spreadsheet. The following data have been inserted for our example: (partial list shown)



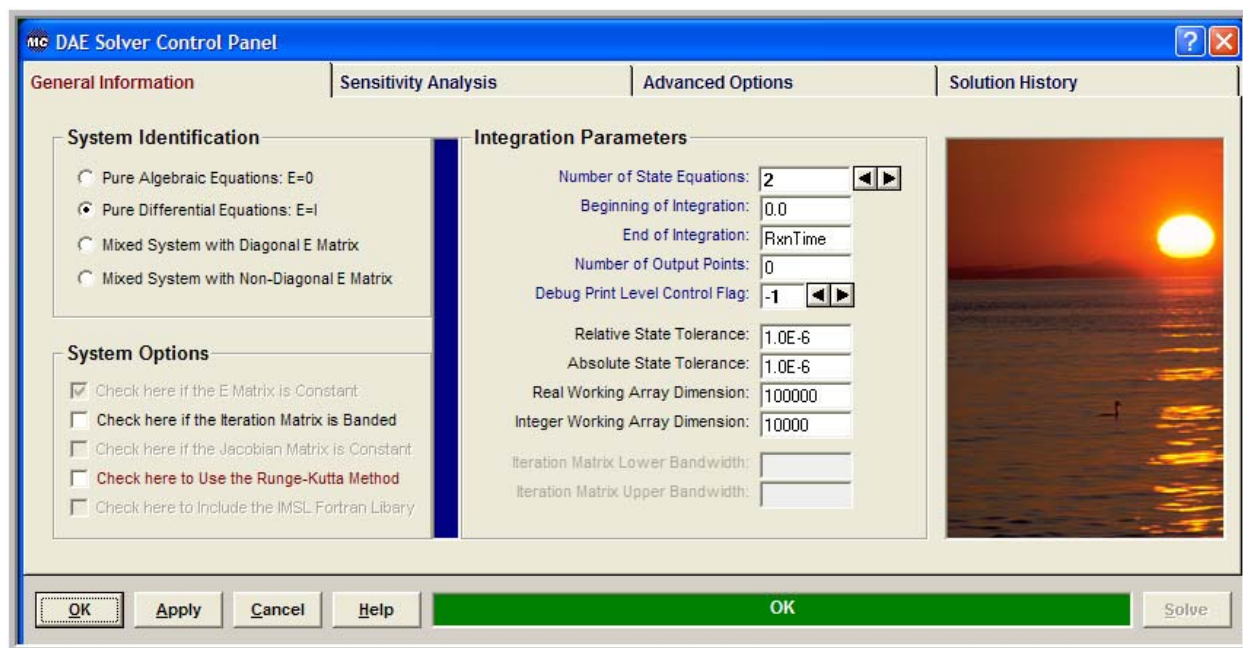
The screenshot shows the 'Parameter Estimation Solver Control Panel' with the 'Experimental Data' tab selected. The table below represents the data entered in the 'Experimental Data' tab.

	RunID	Time	Temp	cAo	cBo	cA	cB	Wu (1)	Wu (2)
1	1	0.00	25.00	1.00	0.50	1.0000	0.5000	1.0	1.0
2	1	0.24	25.00	1.00	0.50	0.8669	0.7075	1.0	1.0
3	1	0.48	25.00	1.00	0.50	0.5590	0.6552	1.0	1.0
4	1	0.71	25.00	1.00	0.50	0.5385	0.8471	1.0	1.0
5	1	0.95	25.00	1.00	0.50	0.3472	0.7031	1.0	1.0
6	1	1.19	25.00	1.00	0.50	0.3345	0.8475	1.0	1.0
7	1	1.43	25.00	1.00	0.50	0.2157	0.6701	1.0	1.0
8	1	1.67	25.00	1.00	0.50	0.2078	0.7796	1.0	1.0
9	1	1.90	25.00	1.00	0.50	0.1340	0.6002	1.0	1.0
10	1	2.14	25.00	1.00	0.50	0.1291	0.6838	1.0	1.0
11	1	2.38	25.00	1.00	0.50	0.0832	0.5177	1.0	1.0
12	1	2.62	25.00	1.00	0.50	0.0802	0.5820	1.0	1.0
13	1	2.86	25.00	1.00	0.50	0.0517	0.4358	1.0	1.0
14	1	3.10	25.00	1.00	0.50	0.0498	0.4855	1.0	1.0
15	1	3.33	25.00	1.00	0.50	0.0321	0.3608	1.0	1.0

Finally you may specify replicate experiments for performing lack-of-fit analysis and model discrimination.

Entering the Information about the Kinetic Model

Now click the **Model** button to enter the information on the differential equations. The *DAE Solver Control Panel* window appears



In the **System Identification** group you will see that the option *Pure Differential Equations E=I* has already been selected for you. From the **Integration Parameters** group enter the *Number of State Equations* the *Beginning* and *End of Integration* (notice that the End of the Integration is equal to $RxnTime=Xu(2)$, the second experimental setting), set *Number of Output Points* equal to zero and change *Debug Print Level Control Flag* to -1 to suppress the printing from the DAE solver during the estimation process. Optionally you may change the *Relative* and *Absolute State Tolerance* fields. The *Real* and *Integer Working Array Dimension* fields are indicative of the size of the problem. If the default values are not large enough the solver will return with the message indicating the space requirements for your problem. You may also need to examine if your model has a banded structure in which case you will have to check the appropriate options in the **System Options** group. After you make all your selections click **OK**. When the Parameter Estimation control panel appears click **OK** and proceed to save and run your model.

Saving and Running

You are now ready to save your model and run it. New files are labeled **UNTITLED** until they are saved. Keep in mind that the maximum number of characters in a line is 132; the maximum number of lines in a file is infinity. In order to save your project:

- From the **File** menu, choose **Save**. This will save your model and create the Fortran code that will access the Parameter Estimation solver. The **Save As** dialog box appears.
- In the Directories box, double-click a directory where you want to store the source file (or down a directories path to the appropriate directory.)
- Type a filename (a filename cannot contain the following characters: \ / : * ? " < > |) in the File Name box, then choose OK. The default extension given to a file is **AVW**.
- To view the Fortran code that you have just created from the **View** menu choose **Fortran Code**.

New files are labeled **UNTITLED** until they are saved. The maximum number of characters in a line is 132; the maximum number of lines in a file is infinity. Before you can save or close a window it must be active. To make a window active, either switch to the window (by clicking anywhere in it) or choose the window name or number from the Window menu.

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 Experiments..... 48
Number of Parameters..... 4
Number of Responses..... 2
Number of Settings..... 5
  
```

EXIT GREGPLUS: SOLUTION FOUND. MODEL No. 1

STATISTICAL ANALYSIS

```

OBJECTIVE FUNCTION..... -2.66465E+02
SUM OF SQUARES OF RESIDUALS..... 1.82052E-01
SUM OF SQUARES OF WEIGHTED RESIDUALS..... 1.82052E-01
ESTIMATED PARAMETERS FROM DATA..... 4
TOTAL OBSERVATIONS DATA COUNT IS..... 96
  
```

PARAMETER	USER ESTIMATES	OPTIMAL ESTIMATES	95% MARGINAL HPD INTERVALS	PARAMETER STATUS
PAR(1)	5.000000E-01	3.505220E-01	3.505220E-01 +- 3.310E-02	Estimated
PAR(2)	1.000000E+01	1.452657E+01	1.452657E+01 +- 1.282E+00	Estimated
PAR(3)	5.000000E-01	-4.532411E-01	-4.532411E-01 +- 3.903E-02	Estimated
PAR(4)	1.000000E+01	9.800838E+00	9.800838E+00 +- 1.504E+00	Estimated

NORMALIZED PARAMETER COVARIANCE MATRIX

```


1.000
0.080 1.000
0.018 -0.012 1.000
-0.013 -0.026 0.011 1.000
  
```

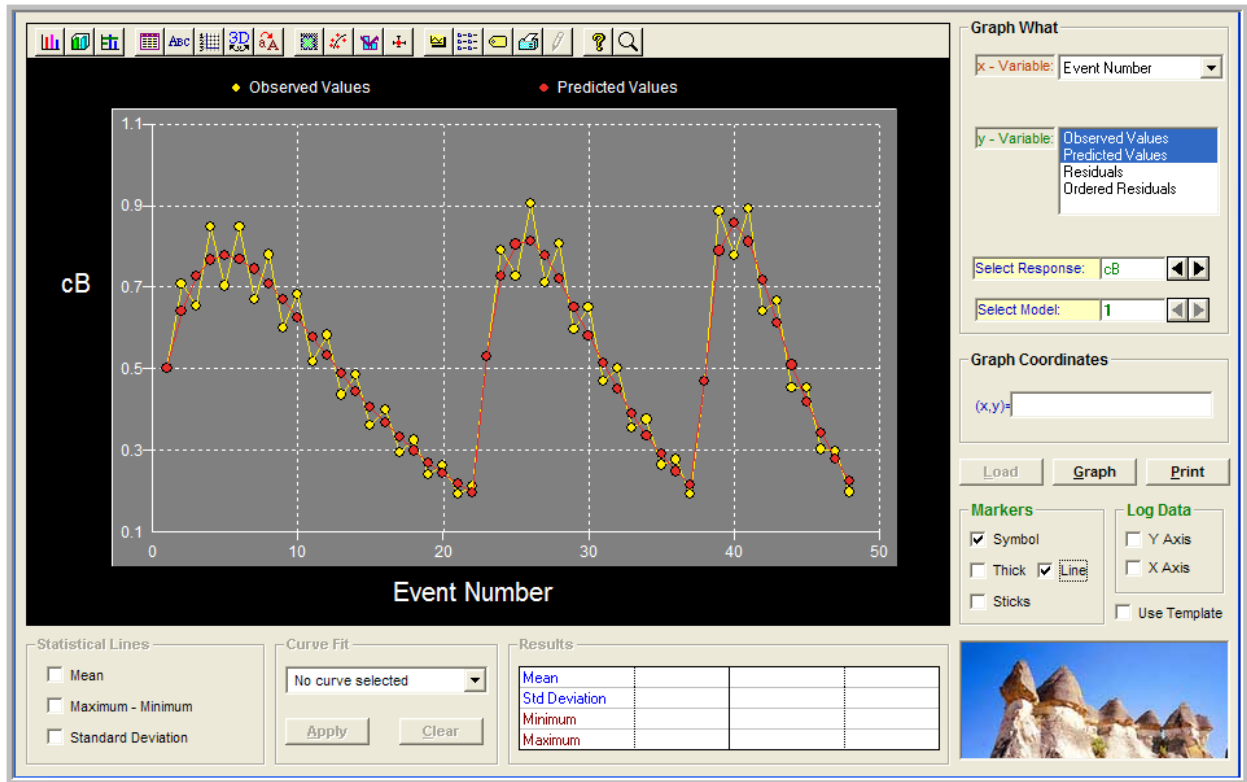
EVENT	OBSERVED	PREDICTED	RESIDUAL
1	1.0000E+00	1.0000E+00	0.0000E+00
2	8.6690E-01	7.8943E-01	7.7474E-02
3	5.5900E-01	6.2319E-01	-6.4191E-02
4	5.3850E-01	4.9683E-01	4.1667E-02
5	3.4720E-01	3.9221E-01	-4.5012E-02
6	3.3450E-01	3.0962E-01	2.4879E-02
7	2.1570E-01	2.4442E-01	-2.8723E-02
8	2.0780E-01	1.9295E-01	1.4847E-02
9	1.3400E-01	1.5383E-01	-1.9830E-02
10	1.2910E-01	1.2144E-01	7.6629E-03
11	8.3200E-02	9.5865E-02	-1.2665E-02
12	8.0200E-02	7.5678E-02	4.5215E-03
13	5.1700E-02	5.9742E-02	-8.0424E-03
14	4.9800E-02	4.7162E-02	2.6379E-03
15	3.2100E-02	3.7600E-02	-5.4995E-03
16	3.0900E-02	2.9682E-02	1.2180E-03
17	1.9900E-02	2.3432E-02	-3.5317E-03
18	1.9200E-02	1.8498E-02	7.0247E-04
19	1.2400E-02	1.4602E-02	-2.2024E-03
20	1.1900E-02	1.1642E-02	2.5822E-04
21	7.7000E-03	9.1904E-03	-1.4904E-03
22	7.4000E-03	7.2552E-03	1.4480E-04
23	9.5000E-01	9.5000E-01	0.0000E+00
24	7.4670E-01	6.4748E-01	9.9219E-02
25	4.1470E-01	4.4129E-01	-2.6595E-02
26	3.4410E-01	3.0561E-01	3.8489E-02
27	1.9110E-01	2.0829E-01	-1.7191E-02
28	1.5860E-01	1.4196E-01	1.6637E-02
29	8.8100E-02	9.6756E-02	-8.6557E-03
30	7.3100E-02	6.5945E-02	7.1554E-03

31	4.0600E-02	4.5669E-02	-5.0688E-03
32	3.3700E-02	3.1126E-02	2.5741E-03
33	1.8700E-02	2.1214E-02	-2.5141E-03
34	1.5500E-02	1.4459E-02	1.0414E-03
35	8.6000E-03	9.8546E-03	-1.2546E-03
36	7.1000E-03	6.7166E-03	3.8337E-04
37	4.0000E-03	4.6515E-03	-6.5155E-04
38	1.0300E+00	1.0300E+00	0.0000E+00
39	5.9690E-01	5.6359E-01	3.3312E-02
40	2.6500E-01	3.0838E-01	-4.3380E-02
41	1.7580E-01	1.7303E-01	2.7699E-03
42	7.8000E-02	9.4677E-02	-1.6677E-02
43	5.1800E-02	5.1805E-02	-4.8473E-06
44	2.3000E-02	2.8346E-02	-5.3462E-03
45	1.5200E-02	1.5510E-02	-3.1036E-04
46	6.8000E-03	8.7030E-03	-1.9030E-03
47	4.5000E-03	4.7622E-03	-2.6220E-04
48	2.0000E-03	2.6058E-03	-6.0581E-04
1	5.0000E-01	5.0000E-01	0.0000E+00
2	7.0750E-01	6.4185E-01	6.5646E-02
3	6.5520E-01	7.2607E-01	-7.0866E-02
4	8.4710E-01	7.6683E-01	8.0266E-02
5	7.0310E-01	7.7906E-01	-7.5956E-02
6	8.4750E-01	7.6918E-01	7.8316E-02
7	6.7010E-01	7.4406E-01	-7.3965E-02
8	7.7960E-01	7.0886E-01	7.0744E-02
9	6.0020E-01	6.6922E-01	-6.9023E-02
10	6.8380E-01	6.2448E-01	5.9317E-02
11	5.1770E-01	5.7836E-01	-6.0657E-02
12	5.8200E-01	5.3235E-01	4.9651E-02
13	4.3580E-01	4.8751E-01	-5.1714E-02
14	4.8550E-01	4.4456E-01	4.0939E-02
15	3.6080E-01	4.0559E-01	-4.4785E-02
16	3.9930E-01	3.6745E-01	3.1846E-02
17	2.9500E-01	3.3204E-01	-3.7039E-02
18	3.2500E-01	2.9937E-01	2.5633E-02
19	2.3920E-01	2.6939E-01	-3.0188E-02
20	2.6260E-01	2.4310E-01	1.9502E-02
21	1.9270E-01	2.1809E-01	-2.5385E-02
22	2.1090E-01	1.9540E-01	1.5502E-02
23	5.3000E-01	5.3000E-01	0.0000E+00
24	7.9050E-01	7.2670E-01	6.3797E-02
25	7.2850E-01	8.0513E-01	-7.6629E-02
26	9.0450E-01	8.1215E-01	9.2347E-02
27	7.1060E-01	7.7775E-01	-6.7146E-02
28	8.0550E-01	7.2016E-01	8.5340E-02
29	5.9720E-01	6.5197E-01	-5.4774E-02
30	6.5070E-01	5.8097E-01	6.9732E-02
31	4.6920E-01	5.1458E-01	-4.5384E-02
32	5.0100E-01	4.4958E-01	5.1422E-02
33	3.5580E-01	3.9022E-01	-3.4422E-02
34	3.7550E-01	3.3701E-01	3.8492E-02
35	2.6430E-01	2.8992E-01	-2.5623E-02
36	2.7710E-01	2.4866E-01	2.8438E-02
37	1.9400E-01	2.1416E-01	-2.0162E-02
38	4.7000E-01	4.7000E-01	0.0000E+00
39	8.8580E-01	7.8877E-01	9.7028E-02
40	7.7770E-01	8.5643E-01	-7.8734E-02
41	8.9160E-01	8.1141E-01	8.0195E-02
42	6.4180E-01	7.1786E-01	-7.6056E-02
43	6.6620E-01	6.1167E-01	5.4535E-02
44	4.5320E-01	5.0960E-01	-5.6404E-02
45	4.5450E-01	4.1863E-01	3.5871E-02
46	3.0250E-01	3.4376E-01	-4.1257E-02
47	2.9910E-01	2.7821E-01	2.0889E-02
48	1.9720E-01	2.2425E-01	-2.7047E-02

NUMBER OF ITERATIONS..... 5
NUMBER OF FUNCTION CALLS..... 30

Graphical Results

If you wish to see various graphs of the estimation process from the *View* menu choose *Solution Graphs*, or click  The Athena Visual Studio graphics control panel appears:



In this window first we click *Load* to load the numerical results. Then in the **Graph What** group we select the **x-variable** (here **Event Number**) and the **y-variables** (here **Observed** and **Predicted Values**) and click *Graph*. You should see the monitoring 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. You may also select to other graphs, like plotting of residuals, plotting observed vs. predicted values, or against any selected settings.

Gradient Vector and Sensitivity Analysis

The gradient vector is defined as the vector of derivatives of the objective function with respect to the model adjustable parameters. For our example there are four adjustable parameters therefore the gradient vector is defined according to the equations shown below:

$$\nabla\Phi(\boldsymbol{\theta}) = \left[\frac{\partial\Phi}{\partial\theta_1}, \frac{\partial\Phi}{\partial\theta_2}, \frac{\partial\Phi}{\partial\theta_3}, \frac{\partial\Phi}{\partial\theta_4} \right]^T$$

The Athena Visual Studio parameter estimation solver calculates these derivatives by numerical perturbation of the adjustable parameters. The perturbation step size is optimized by the solver in order to minimize the round-off and truncation errors. The numerical calculation of the gradient vector is usually time consuming especially for large sets of experimental data or large number of differential equations. For each perturbation the system of the differential equations has to be solved for the entire set of the experimental data.

Alternatively we can use the theory of sensitivity analysis for differential equations and compute the gradient vector of the objective function analytically. To do that, first observe that the relation between the model adjustable parameters that we are estimating and the reaction rate constants is given by the following equations:

$$\begin{aligned} \ln k_1 &= \theta_1 + \alpha\theta_2 & \alpha &= 1 - \frac{T_B}{T} \\ \ln k_2 &= \theta_3 + \alpha\theta_4 \end{aligned}$$

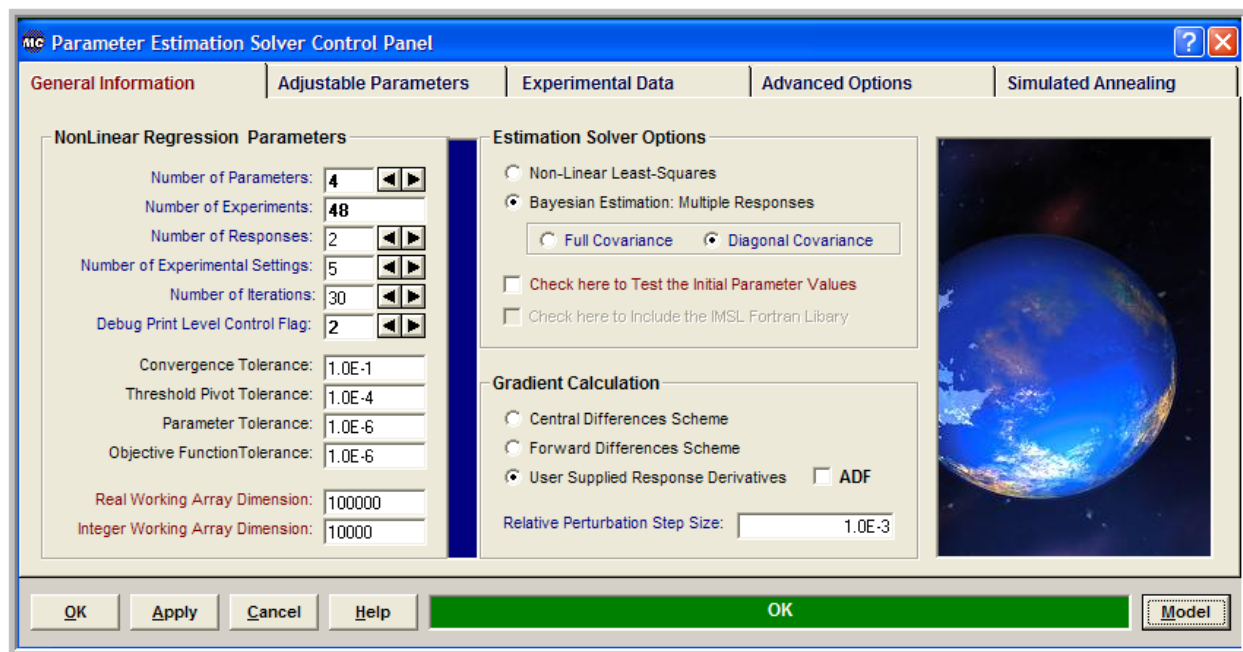
Therefore we obtain the following equations for the components of the gradient vector:

$$\begin{aligned} \frac{\partial\Phi}{\partial\theta_1} &= \frac{\partial\Phi}{\partial\ln k_1} = \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{e}(\mathbf{u})}{\partial\ln k_1} = -\frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{y}}{\partial\ln k_1} = -\frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{u}}{\partial\ln k_1} \\ \frac{\partial\Phi}{\partial\theta_2} &= \alpha \frac{\partial\Phi}{\partial\ln k_1} = \alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{e}(\mathbf{u})}{\partial\ln k_1} = -\alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{y}}{\partial\ln k_1} = -\alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{u}}{\partial\ln k_1} \\ \frac{\partial\Phi}{\partial\theta_3} &= \frac{\partial\Phi}{\partial\ln k_2} = \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{e}(\mathbf{u})}{\partial\ln k_2} = -\frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{y}}{\partial\ln k_2} = -\frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{u}}{\partial\ln k_2} \\ \frac{\partial\Phi}{\partial\theta_4} &= \alpha \frac{\partial\Phi}{\partial\ln k_2} = \alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{e}(\mathbf{u})}{\partial\ln k_2} = -\alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{y}}{\partial\ln k_2} = -\alpha \frac{\partial\Phi}{\partial\mathbf{e}(\mathbf{u})} \frac{\partial\mathbf{u}}{\partial\ln k_2} \end{aligned}$$

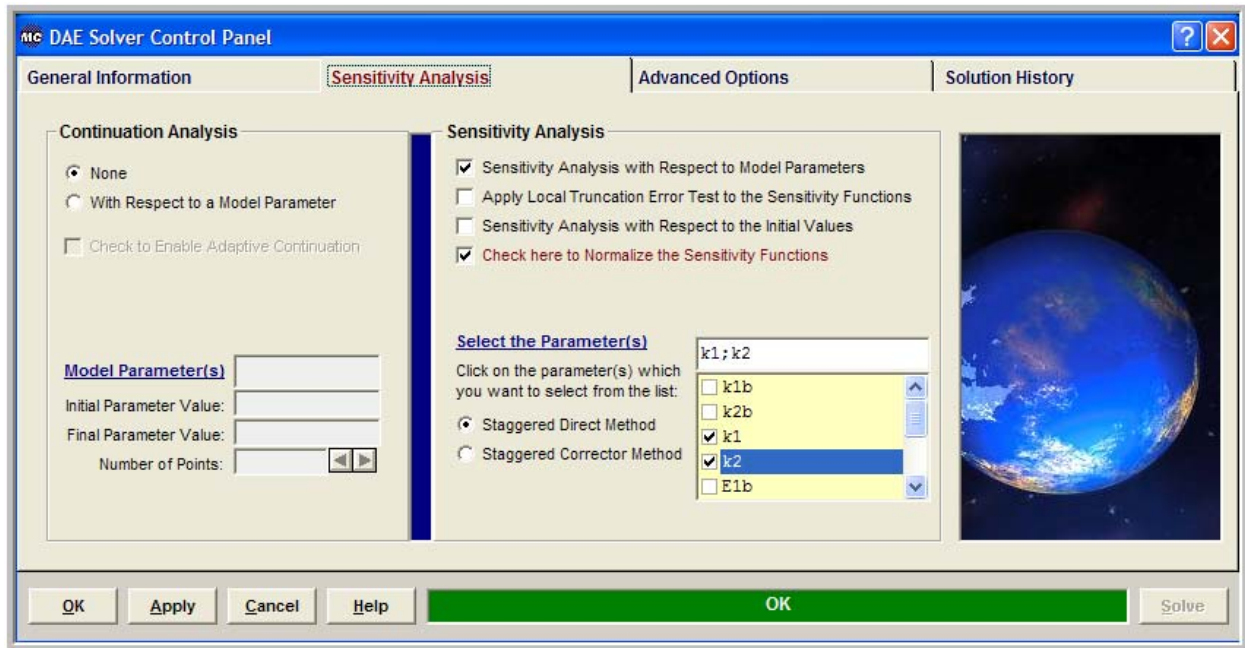
where $\mathbf{e}(\mathbf{u})$ is the residual vector, defined as the observed minus the predicted values vectors. The derivatives of the objective function with respect to the residual vector are calculated internally by the Athena parameter estimation solver. This calculation depends on the type of objective function used for the parameter estimation process (weighted least-squares for single-response or Bayesian estimation for multi-response). The remaining derivatives,

$$\frac{\partial \mathbf{y}}{\partial \ln k_1} = \frac{\partial \mathbf{u}}{\partial \ln k_1} \quad \text{and} \quad \frac{\partial \mathbf{y}}{\partial \ln k_2} = \frac{\partial \mathbf{u}}{\partial \ln k_2}$$

are simply the first order sensitivity coefficients of the state vector $\mathbf{u}(t)$ with respect to the reaction rate constants. These can be calculated either by numerical perturbation as it was done before in this tutorial, or by activating the sensitivity analysis option. In order to do we first load the solver (**Hit F12**). The Parameter Estimation Control Panel appears:



In the **Gradient Calculation** group we select *User Supplied Response Derivatives* and then click the **Model** control button. The **DAE Solver Control Panel** appears:



We then select the **Sensitivity Analysis** tab. In the **Sensitivity Analysis** group we first click *Sensitivity Analysis with Respect to Model Parameters* and also *Check here to Normalize the Sensitivity Functions*. Next from the drop down menu we select the reaction rate constants k_1 and k_2 . This action will force the DAE Athena solver to solve the differential equations and also calculate when needed the first order sensitivity coefficients:

$$\frac{\partial \mathbf{u}}{\partial \ln k_1} \quad \text{and} \quad \frac{\partial \mathbf{u}}{\partial \ln k_2}$$

We now click **OK** to unload the Athena solvers and hit **F11** to enter the section for the Gradient Vector. For our example we enter the code shown below:

@Gradient Vector

```

dY(1:2,1)=U(1:2,2)
dY(1:2,2)=U(1:2,2)*(1.0-Tb/Temp)

dY(1:2,3)=U(1:2,3)
dY(1:2,4)=U(1:2,3)*(1.0-Tb/Temp)

```

We are now ready to build and execute the parameter estimation problem. If we do that, we obtain exactly the same numerical results as before by we now observe that the number of function (model) call drops from 30 to 10. This results in a reduction of the computer execution time by a factor of three which is a considerable amount especially for very large problems.

Note: Please read the **Differential Equations Tutorial** or the **Athena Knowledge Base** for detailed information on how the Athena solvers store the first order sensitivity functions.