ChemSep Tutorial: Phase Equilibrium Calculations

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In this document we illustrate the use of *ChemSep* by considering its use to solve some example problems posed in thermodynamics textbooks. The examples considered below are:

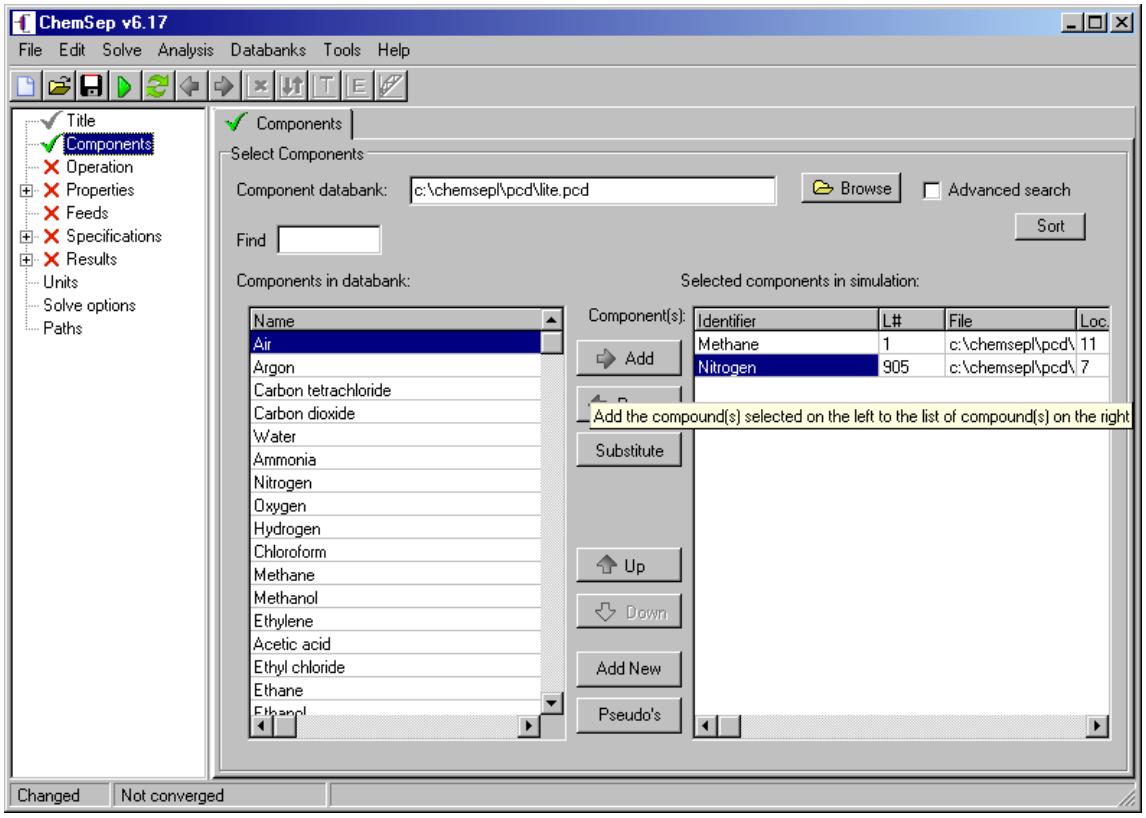
1. Estimating K-values from the Peng-Robinson Equation of State (this is Example 10.2 in *Introductory Chemical Engineering Thermodynamics*, by J.R. Elliott and C.T. Lira (Prentice-Hall, 1999).

2. Creating a phase diagram for methanol-benzene (this is Example 10.8 in the same book).

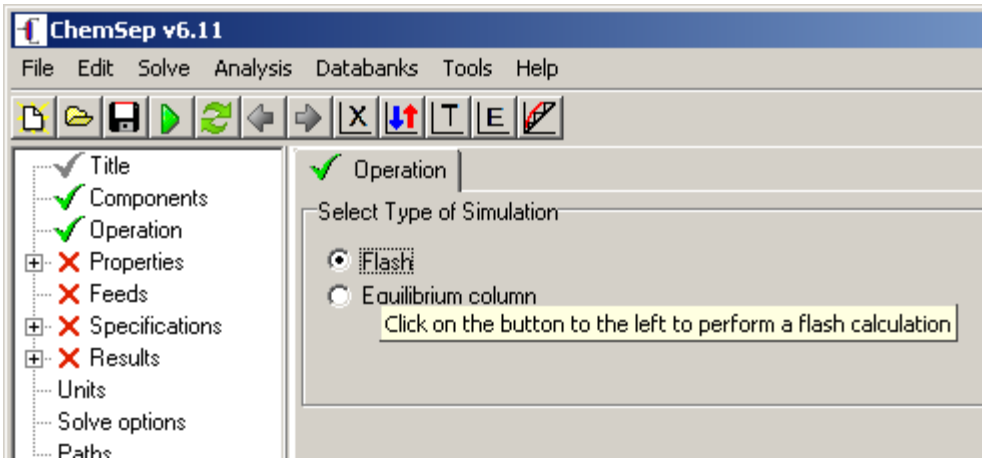
Tutorial 1: K-values from the Peng-Robinson Equation of State

The bubble point pressure of an equimolar mixture of nitrogen(1) and methane(2) at a temperature of 100 K is to be calculated using the Peng-Robinson equation

We begin by starting *ChemSep* and selecting nitrogen and methane from the databank.

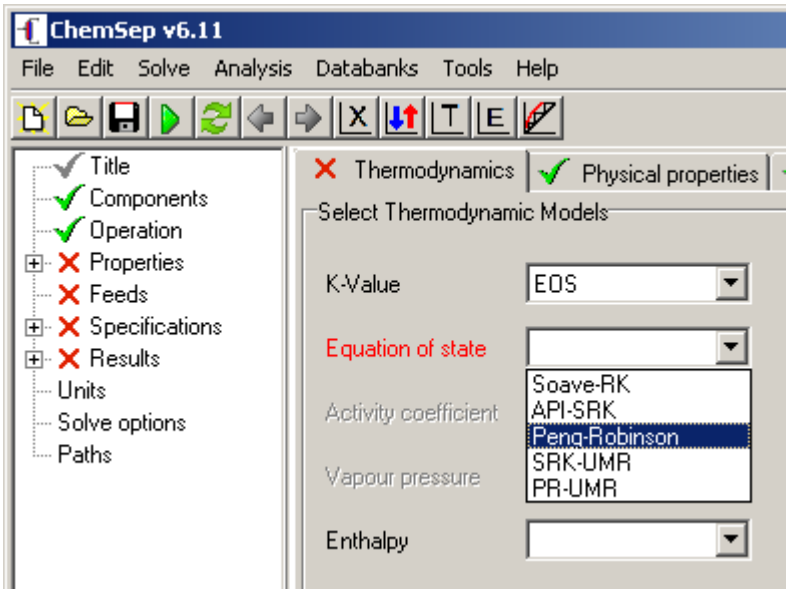


Next select the **Operation** tab and choose **Flash**



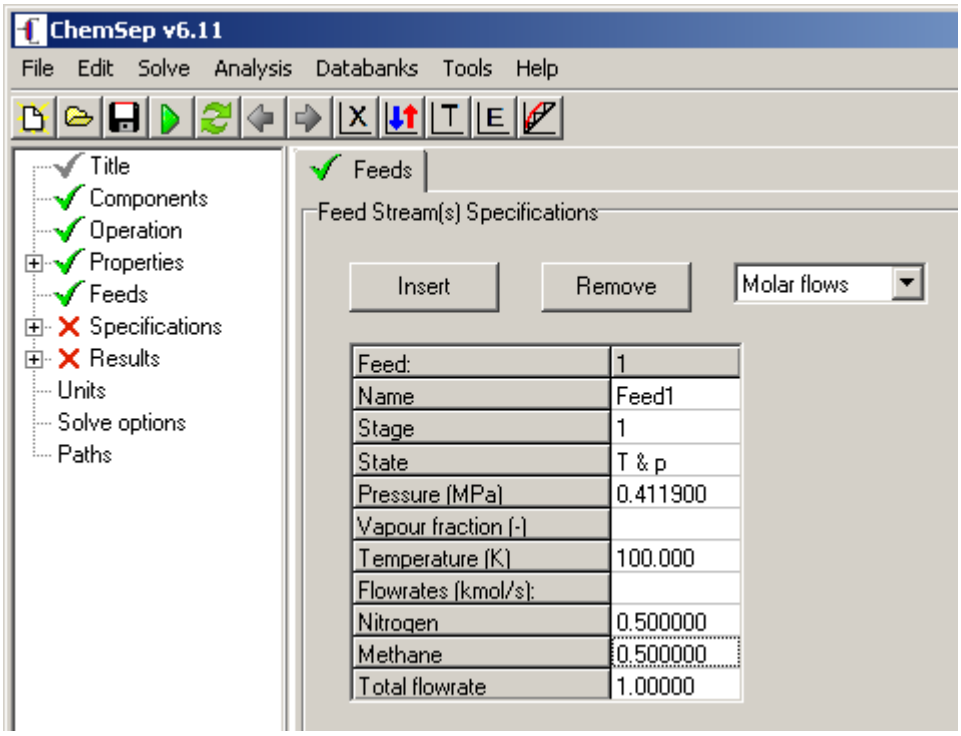
The next step is to select the appropriate thermodynamic models. It is beyond the scope of this tutorial to explain *how* to choose appropriate models (it must suffice to note that the proper selection of thermodynamic models is of central importance in phase equilibrium calculations).

The screen shot below shows the models selected for this exercise.



No enthalpy model is needed for this exercise (we are not interested in that calculation this time), but we selected the Peng-Robinson model there as well.

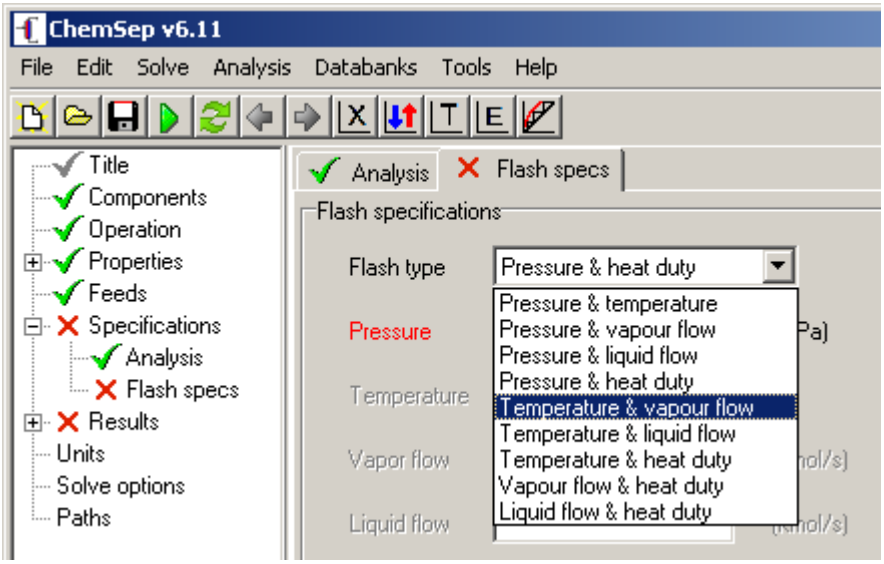
The next step is to specify the composition of the mixture. This is done in the feed panel:



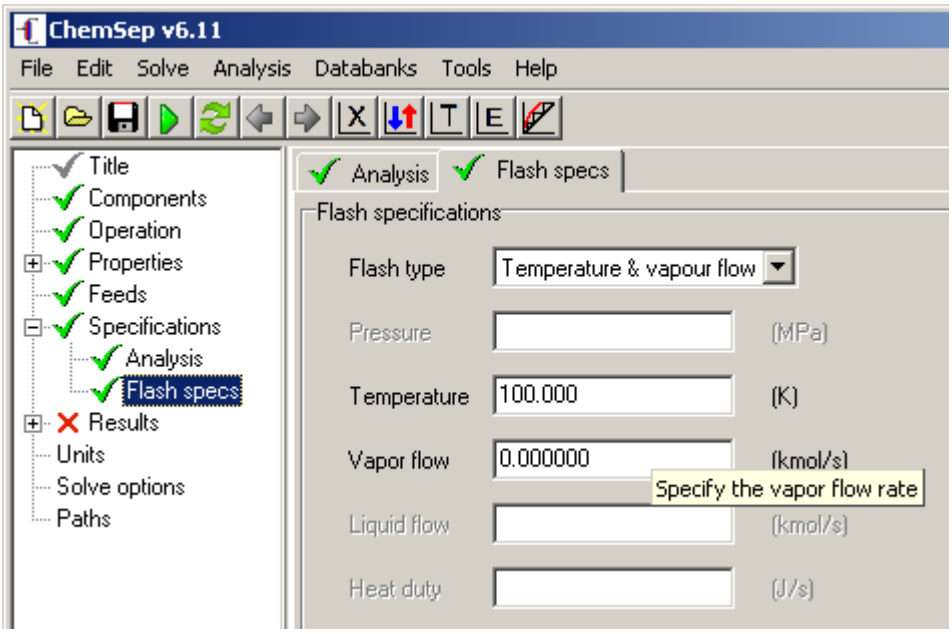
The feed panel asks for component flows, but what matters to us is the composition and not the flows. Accordingly, we simply set the component flows equal to the corresponding mole fractions.

Note that the feed pressure and temperature are not that important in this calculation. We will set the pressure at which the calculation is to be done in the Flash Specifications panel.

The first task is to select the type of flash calculation that we wish to perform. There are several different flash types available in ChemSep. To determine the bubble point pressure we need to specify the temperature and vapor flow as indicated by the image below.

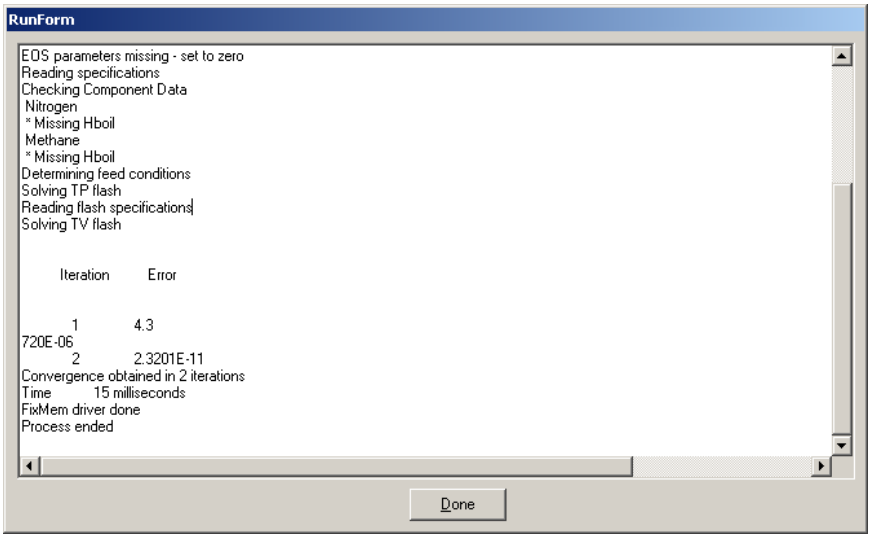


We now set the temperature (to the desired value of 100 K) and the vapor flow to zero (corresponding to a bubble point calculation).

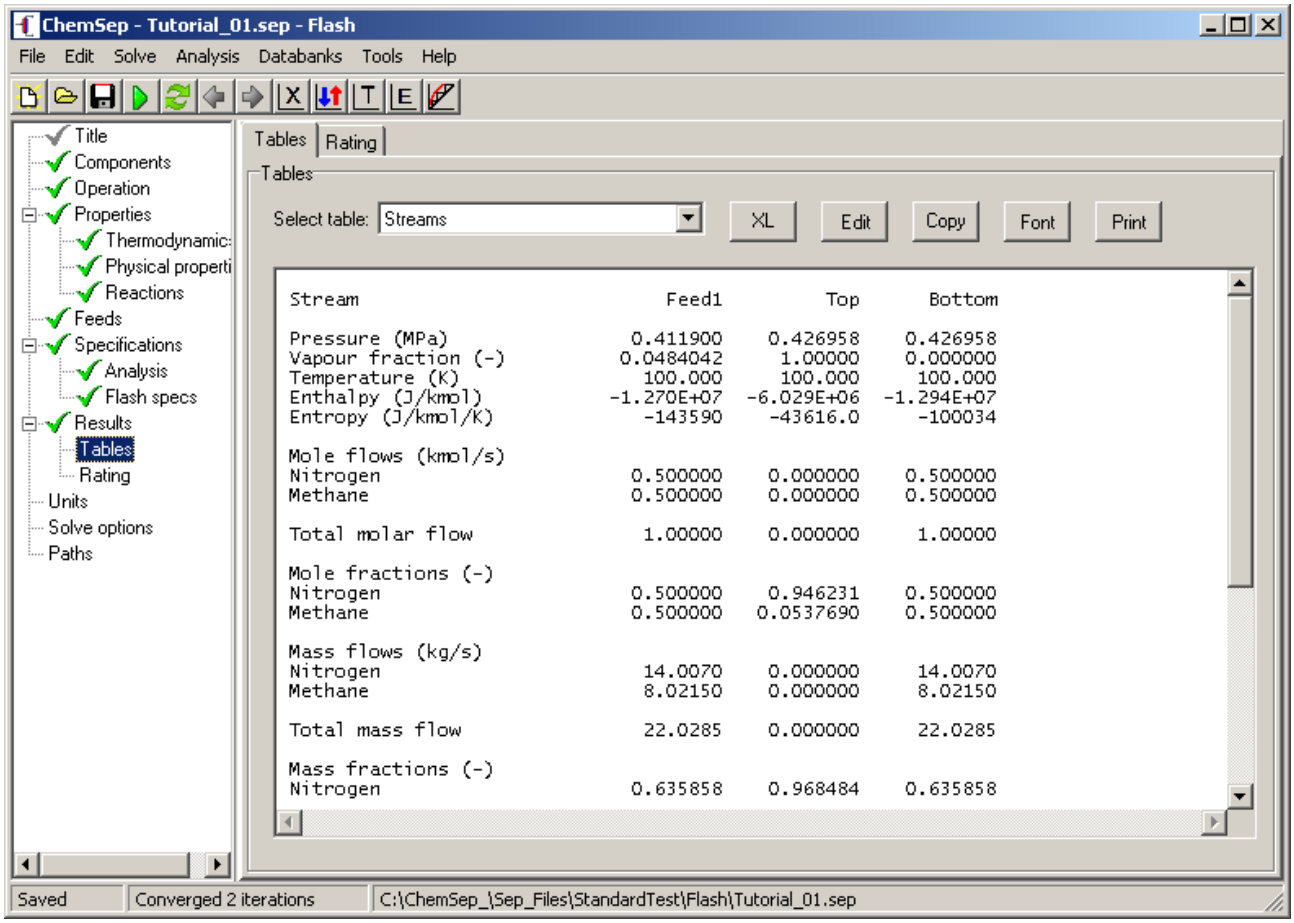


The problem specifications now are complete and we can proceed to solve the problem. First we save the file (using the **File** menu – note that the file name appears on the blue bar at the top of the ChemSep window) and then click on the green arrow head icon to start the calculations.

This will bring up the solve window – which very soon (this is an easy problem) looks like this:

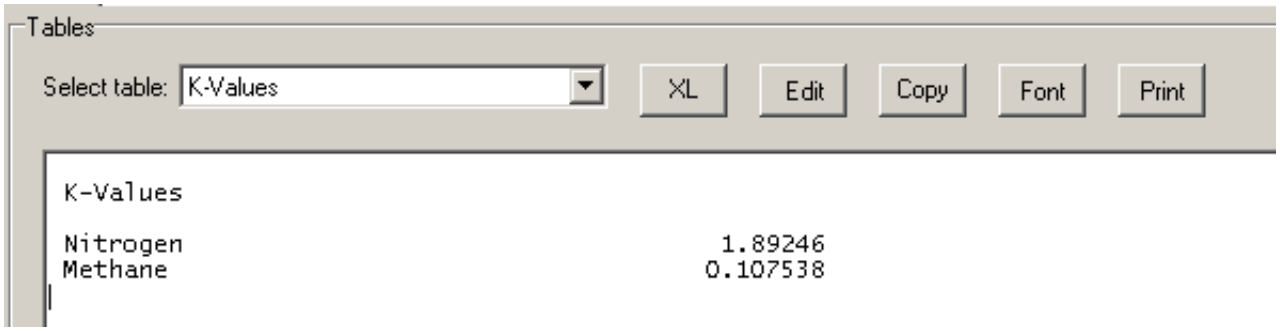


Click on **Done** to close the window and bring up the results panel.



We from this screen shot that the bubble point pressure has been estimated to be 0.427 MPa (Elliott and Lira report that the pressure is close to 0.428 Mpa but their calculation is not converged as tightly as is the one here).

The K-values at the specified temperature (and calculated pressure) can be found in another table:

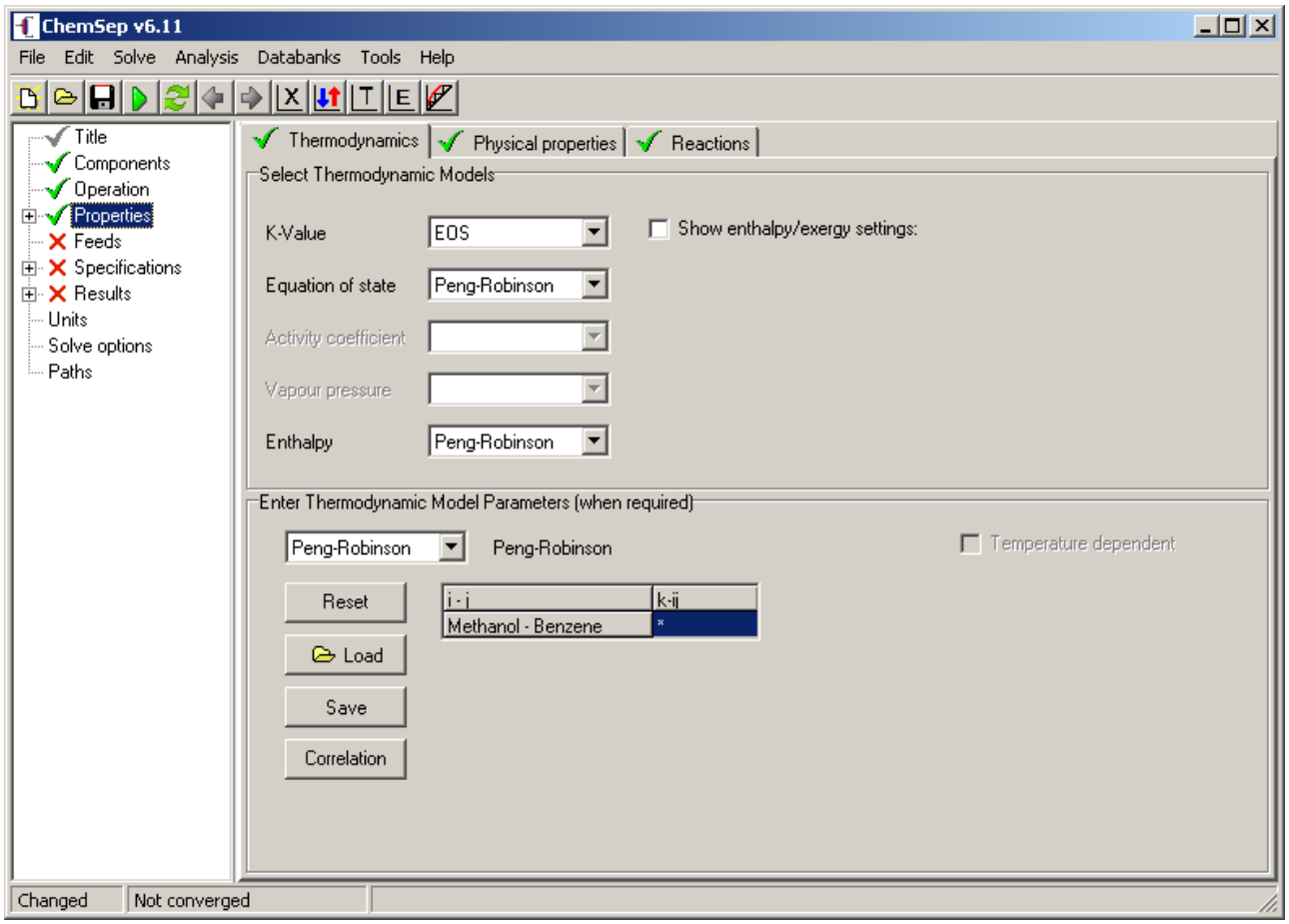


The K-values given by Elliott and Lira are $K_1 = 1.890$ and $K_2 = 0.1073$ (remember that their calculation is not fully converged).

Tutorial 2: Phase Diagram for Methanol – Benzene from a Cubic Equation of State

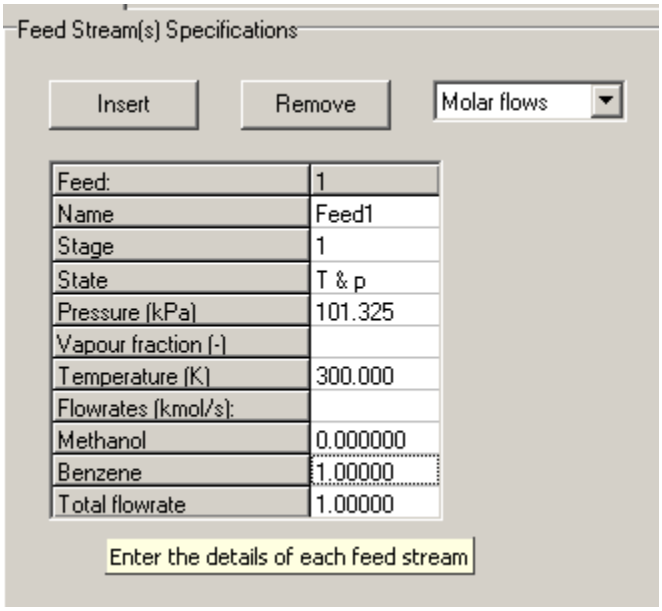
Our second example (which happens to be Example 10.8 in Eliiott and Lira) concerns the creation of a phase diagram for Methanol and Benzene at atmospheric pressure.

We start by selecting methanol and benzene on the **components** panel. Then select **Flash** as before on the **Operation** panel. Use the following **thermodynamic model**:

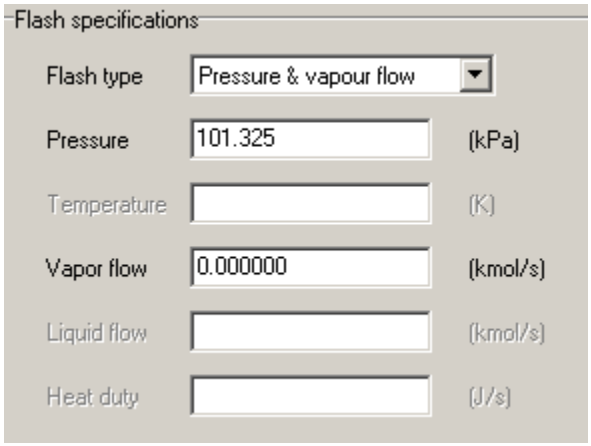


Note the bottom half of this page where we can enter model parameters as required. In this case the interaction parameter is 0.084 and that value must be typed in the space occupied by the * in the image above (the * will be assumed to be zero in this case – but be warned that a * means the default value is taken and that is not always zero).

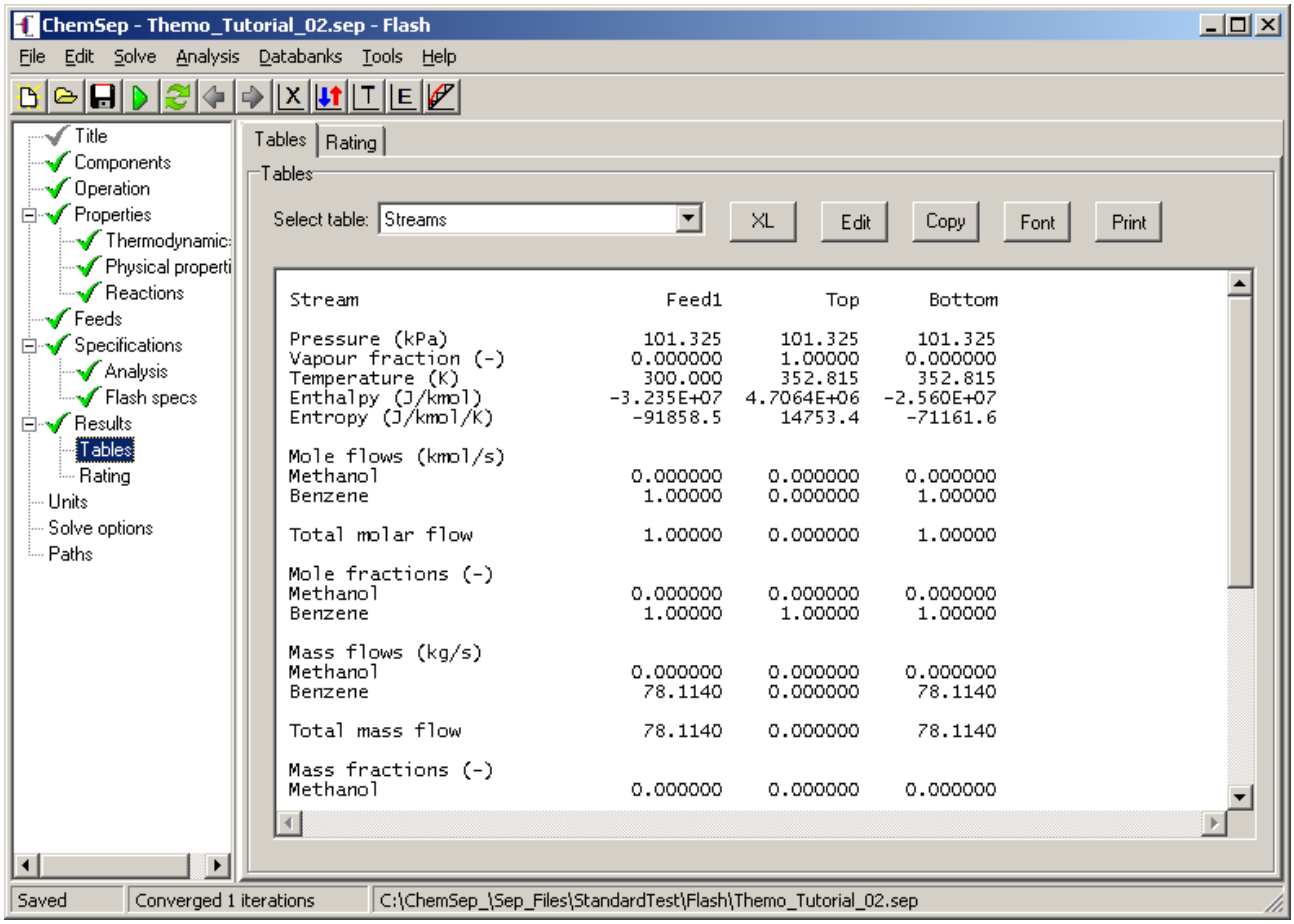
The feed composition is not so important here because, in order to create a phase diagram, we need to perform many calculations at different compositions. In this case, however, we start with a "mixture" that is pure benzene (component 2):



Specify the pressure at which the phase diagram is to be determined (on the **Flash Specifications** panel) and the vapor flow (here set to zero to indicate that we are doing a bubble point calculation).



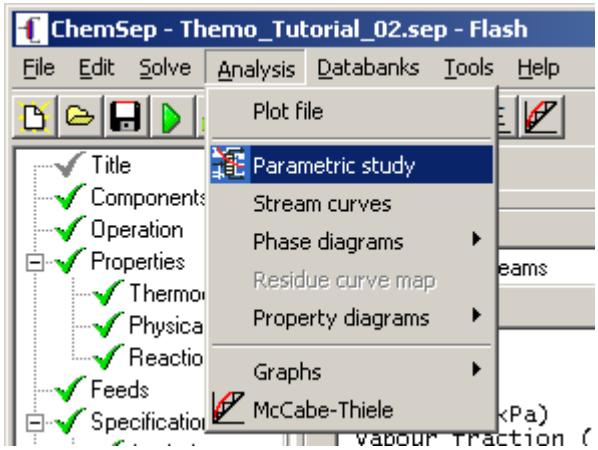
Save the file (under the **File**) menu and Solve it (click on the green arrow head icon and then click on **Done** in the calculation window) to bring up the results page:



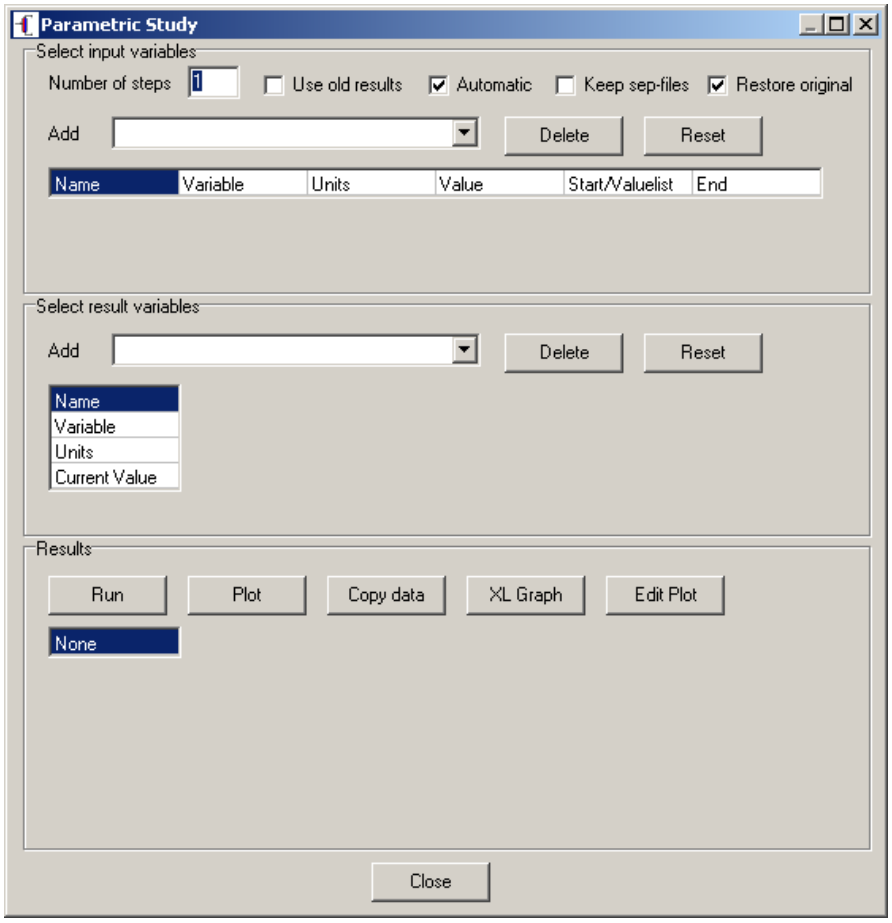
This page tells us that (according to the PR EOS), benzene boils at a temperature of 352.8 K. This is close to the experimental value of 353.25 K).

To prepare a Txy diagram we need to carry out many such calculations at different feed compositions. *ChemSep* has a parametric study option that can make it quite easy to carry out many similar calculations.

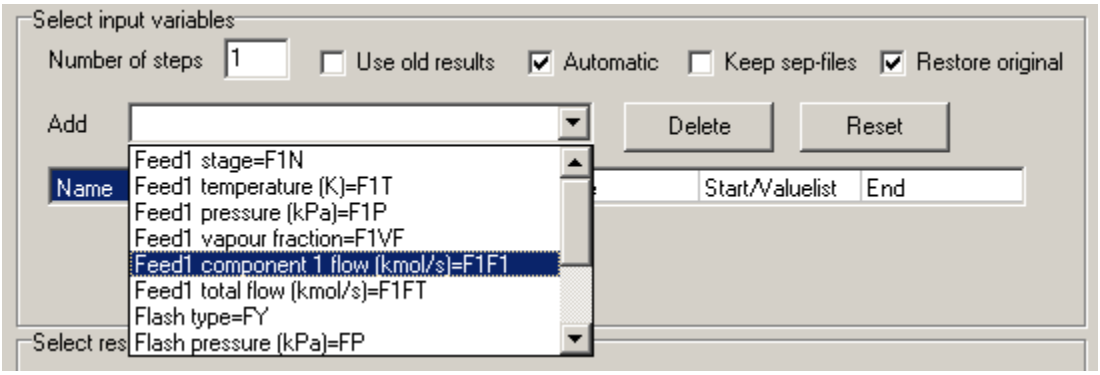
Go to **Analysis** (on the main menu bar) and select **parametric study**.



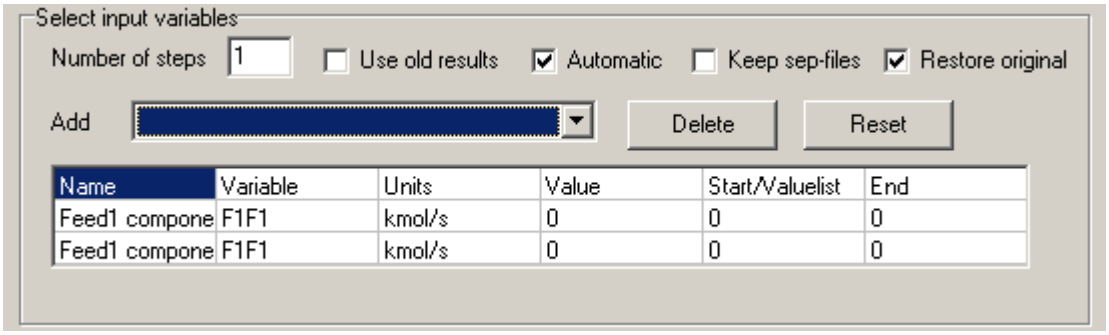
This brings up the following screen:



Click on **Add** and select **Feed component 1 flow** as shown below.

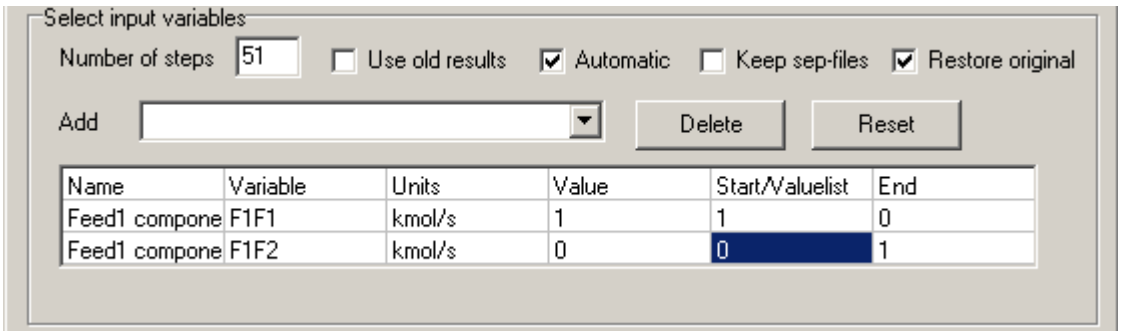


Repeat this step and select **Feed component 1 flow** a second time (there will be warning that you should not select the same variable twice). Clear this warning because this is exactly what you must do at this stage. The top portion of the screen now looks like this:



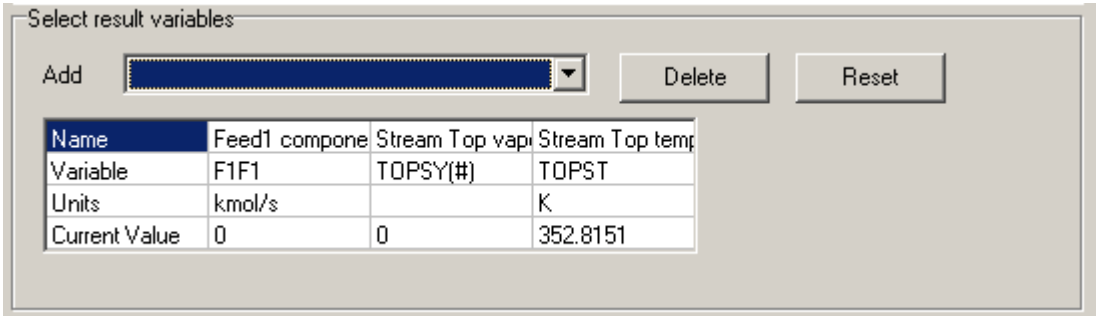
It does not, of course, make sense to vary the same variable more than once at the same time; we are now going to change the second one. Click on the box above where you can read **F1F1** (which means Flow 1, component 1). Retype the string so that it reads **F1F2** (for Flow 1, component 2).

In addition, change the start and end values of both variables as shown in the image below:

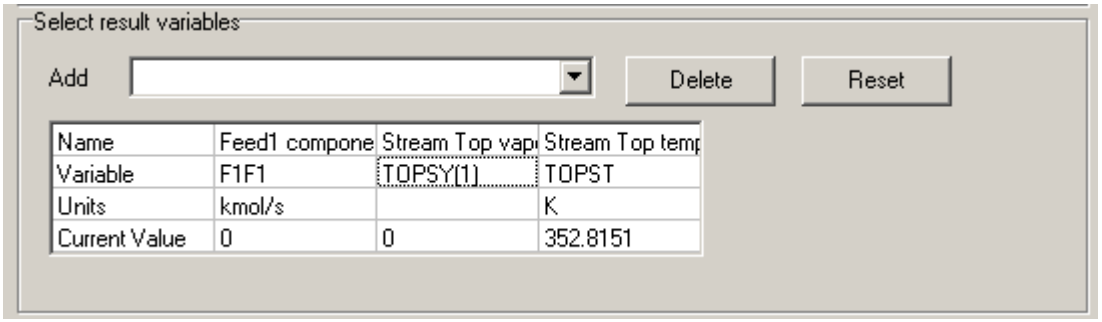


Now, when the parametric study is run it will vary the amount of methanol in the feed (from one to zero) and the amount of benzene in the feed (from 0 to 1) in such a way that the total amount remains the same (1).

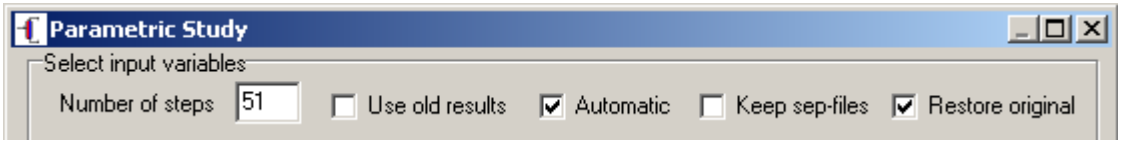
The next step is to select the results variables. For a Txy diagram we need the temperature and the mole fraction of methanol in the vapor phase. Use the drop down list in the center part of the Parametric study window to select these variables and so that this part of the window appears as shown below:



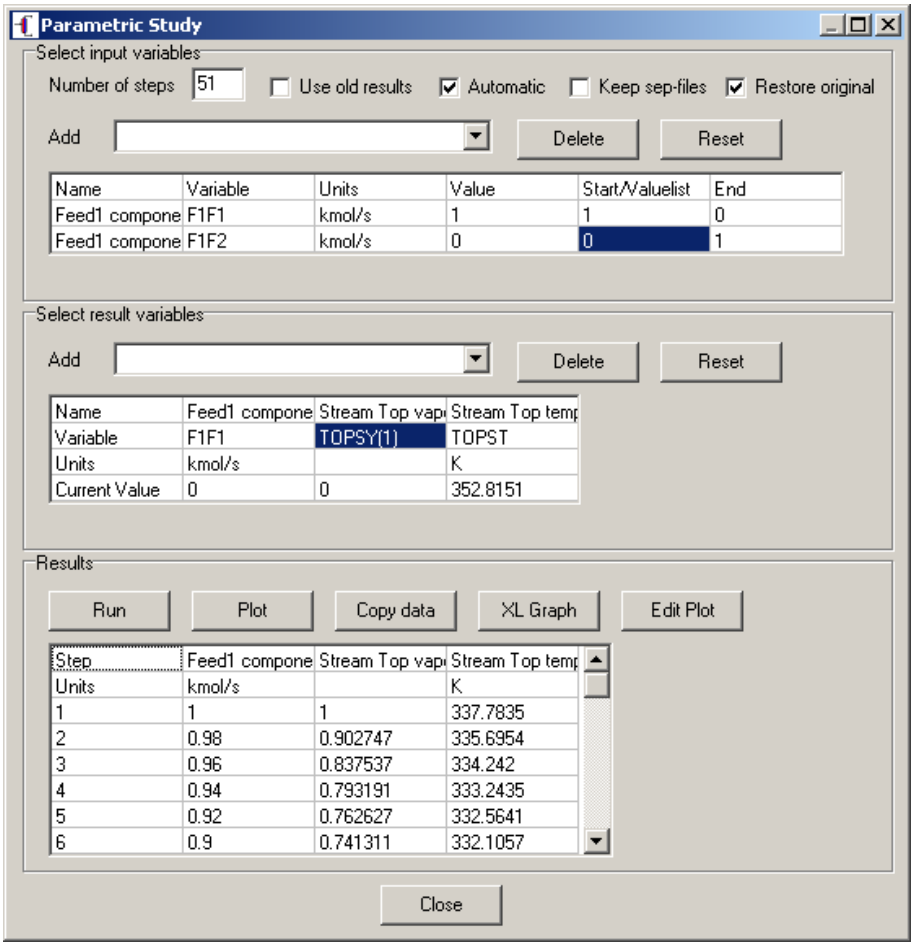
The # sign must be replaced by the number for methanol (1 in this case). Click on that box and replace the # sign by 1:



We are almost ready to run the parametric study. First, select the number of steps we want to cover the range of mole fractions. Enter this number in the space provided near the top of the window.

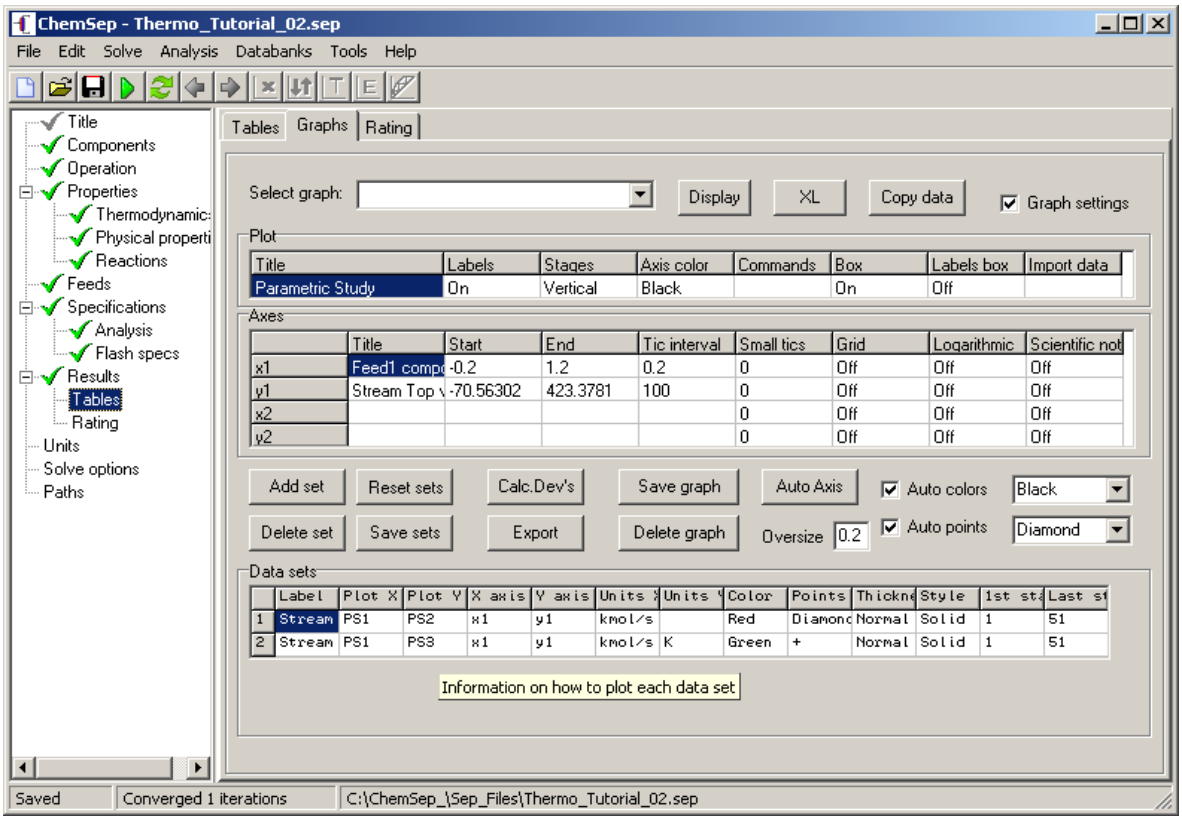


Now click **Run** (near the foot of the window). *ChemSep* will now run through a series of closely related problems as it varies the specified variables (feed mole fractions in this case) over the specified range (0-1 and 1-0 in this case). When completed you will see the window look something like this:

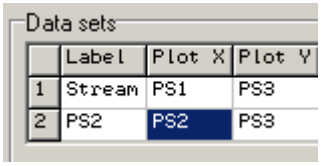


We can plot the results in several different ways using either the plotting capabilities built into *ChemSep* or by using an alternative software package.

First, we show how to display the Txy diagram using the plotting capabilities built into *ChemSep*. If we click on the the **Plot** button *ChemSep* will plot the parametric study results using the first variable that was varied on the X axis (that would be the mole fraction of methanol here) and *all* other variables on the y-axis (that includes both the mole fraction of methanol in the vapor and the temperature). Consequently the diagram will not be exactly what we want to see (which is why we don't show it here). Instead of clicking on **Plot** we suggest that you click on the **Edit Plot** button ; this will bring up the panel shown below.

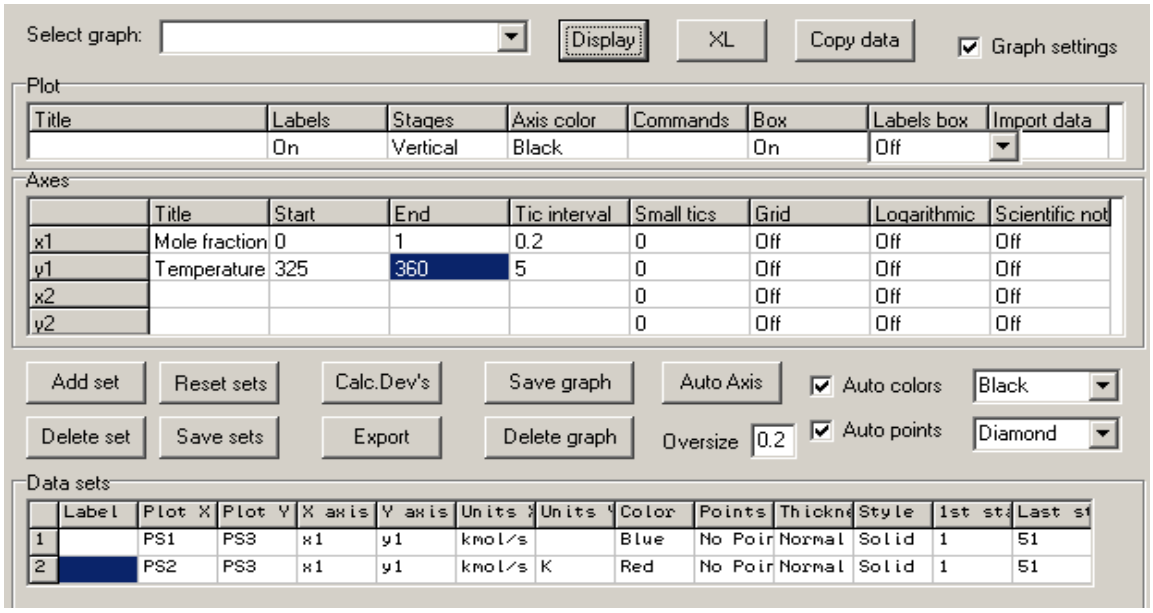


Note the lowest part of this panel headed **Data sets**. *ChemSep* uses the labels PSx (where x is a number) to refer to the columns of results obtained in the Parametric Study. As already noted above *ChemSep* is programmed to display PS2 (the mole fraction of methanol in the vapor) as a function of PS1 AND PS3 (temperature) as a function of PS1. We need to change these settings. Click in the Plot X and Plot Y cells and retype the entries so that this section appears as shown below.

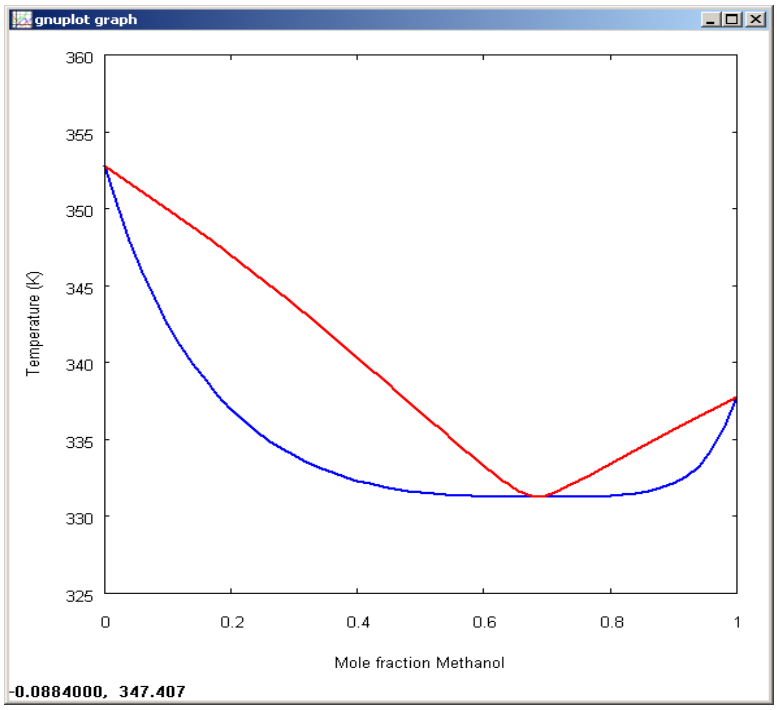


Next, set the axis limits (the quick way is to click on **Auto Axis** but we would recommend adjusting at least the x-axis limits to vary from 0-1). The plot and axis titles can also be changed (click in the appropriate cells and type the names that you prefer). In the screen shot below we show that the plot title was removed, The axis labels were changed to better represent the variable names, the

data set labels were deleted, the default plot colors were changed and the plotting of points was suppressed (leaving only the line joining the points).



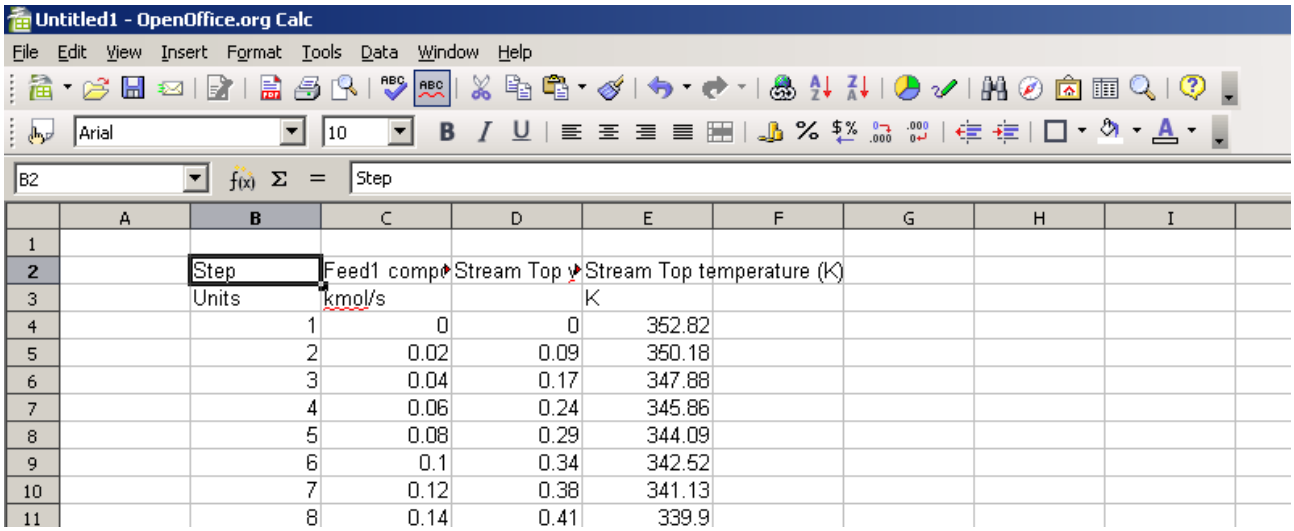
Finally, we click on the **Display** button near the top of this panel to bring up the Txy diagram in a separate window.



It is also possible to add actual experimental data to this plot, detailed instructions on how to do this can be found on the *ChemSep* web site:

www.chemsep.com/downloads/source/VLE_Data/howto_vle/howto_vle.html

Another option is to use some other package that can create plots such as a spreadsheet program. Click on the **Copy Data** button, open a spreadsheet program and paste the data into an open worksheet. Here we use ***OpenOfficeCalc*** (free from www.openoffice.org) to illustrate.



	A	B	C	D	E	F	G	H	I
1									
2		Step	Feed1 comp	Stream Top y	Stream Top temperature (K)				
3		Units	kmol/s		K				
4		1	0	0	352.82				
5		2	0.02	0.09	350.18				
6		3	0.04	0.17	347.88				
7		4	0.06	0.24	345.86				
8		5	0.08	0.29	344.09				
9		6	0.1	0.34	342.52				
10		7	0.12	0.38	341.13				
11		8	0.14	0.41	339.9				

Column C contains the mole fraction of methanol in the liquid, column D has the vapor mole fraction and the temperature is in column E.

Now we can use the plotting capabilities of *OpenOfficeCalc* to create the Txy diagram shown below.