

How to Model Vapor-Liquid Equilibria (VLE) Data with ChemSep

Here we will explain you how you make your comparisons with VLE data with activity coefficient models using ChemSep (LITE) (available free from www.chemsep.com). We will illustrate by trying to model the VLE of a mixture of acetone and benzene.

Selecting the components

When we want to compare the VLE data to predicted values by thermodynamic models we need to define the components as well as make a model selection and provide the interaction parameters for the models. Select "Components" in the tree of the input navigator on the left hand side. This will open a pane where we can select the compounds. ChemSep shows the compounds in the default component library (a "PCD" file) and you can select any of these by double-clicking a compound. Typing a (part of a) name in the "find" box will narrow down the list of components to only those with the particular string in the name. Select Acetone and then Benzene:

ChemSep (TM) v7.30

File Edit Solve Analysis Databanks Tools Help

Component databank: h:\ChemSep\data\pcd\chemsep1.pcd Browse Advanced search

Find ChemSep v7.30 pure component data - Copyright (c) Harry Kooijman and Ross Tayl... Sort

Components in databank:

Name
Air
Argon
Bromine
Carbon tetrachloride
Carbon monoxide
Carbon dioxide
Carbon disulfide
Phosgene
Trichloroacetyl chloride
Hydrogen chloride
Chlorine
Hydrogen iodide
Hydrogen
Water
Hydrogen sulfide
Ammonia

Selected components in simulation:

Identifier	L#	File	Loc.
Acetone	1051	h:\chemsep\data\p 62	
Benzene	501	h:\chemsep\data\p 125	

Separate Apparent and True species

Changed Not converged

Selecting the thermodynamic model(s)

Next we click on the "properties" in the input navigation tree to select the thermodynamic models. For nonideal systems such as the system at hand an activity coefficient model is needed to represent the non-ideality of the liquid mixture. The resulting model for the K-values is called the DECHEMA model, since it is also used in the DECHEMA data book series. As activity model we will first select a predictive model, UNIFAC, which will require no further input. As vapor pressure model we select the Antoine model.

The screenshot shows the ChemSep (TM) v7.30 software interface. The left-hand navigation tree is expanded to 'Properties', with 'Thermodynamic' selected. The main window displays the 'Select Thermodynamic Models' section with the following settings:

- K-value: DECHEMA
- Equation of state: Ideal gas law
- Activity coefficient: UNIFAC
- Vapour pressure: Antoine
- Enthalpy: Excess
- Reference state: Vapour, 298.1 (K)
- Heat of formation: Excluded
- Surroundings T: 298.150 (K)
- Heat Capacity IG: T correlation
- Heat Capacity L: Molar average
- Henry's law components:

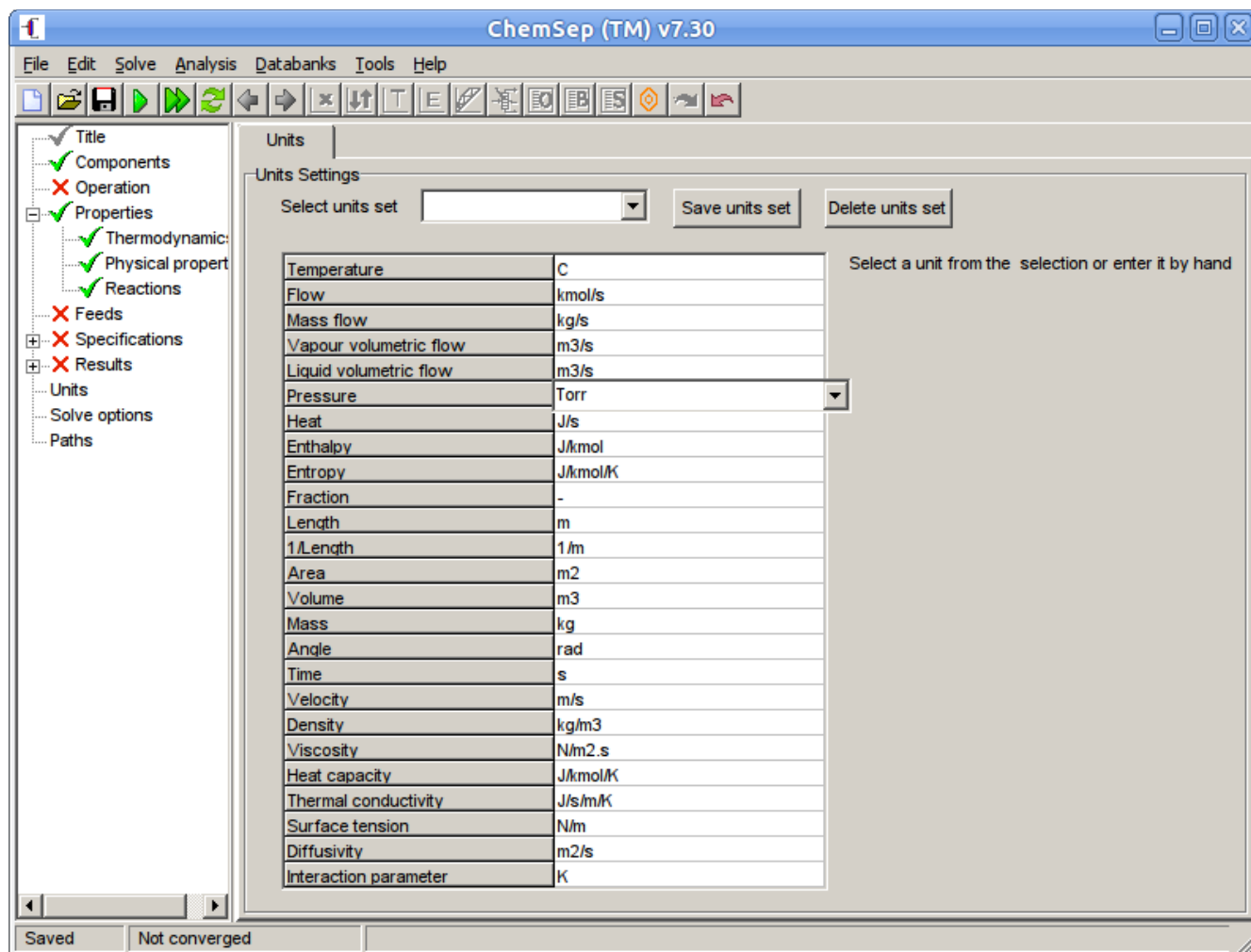
Below this, the 'Enter Thermodynamic Model Parameters (when required)' section is active for UNIFAC. It shows a table of parameters:

Sub-Group	Main-Group	R-i	Q-i
CH3	CH2	0.901100	0.848000
CH3CO	CH2CO	1.67240	1.48800
ACH	ACH	0.531300	0.400000

The status bar at the bottom indicates 'Changed' and 'Not converged'.

Specifying units of measure

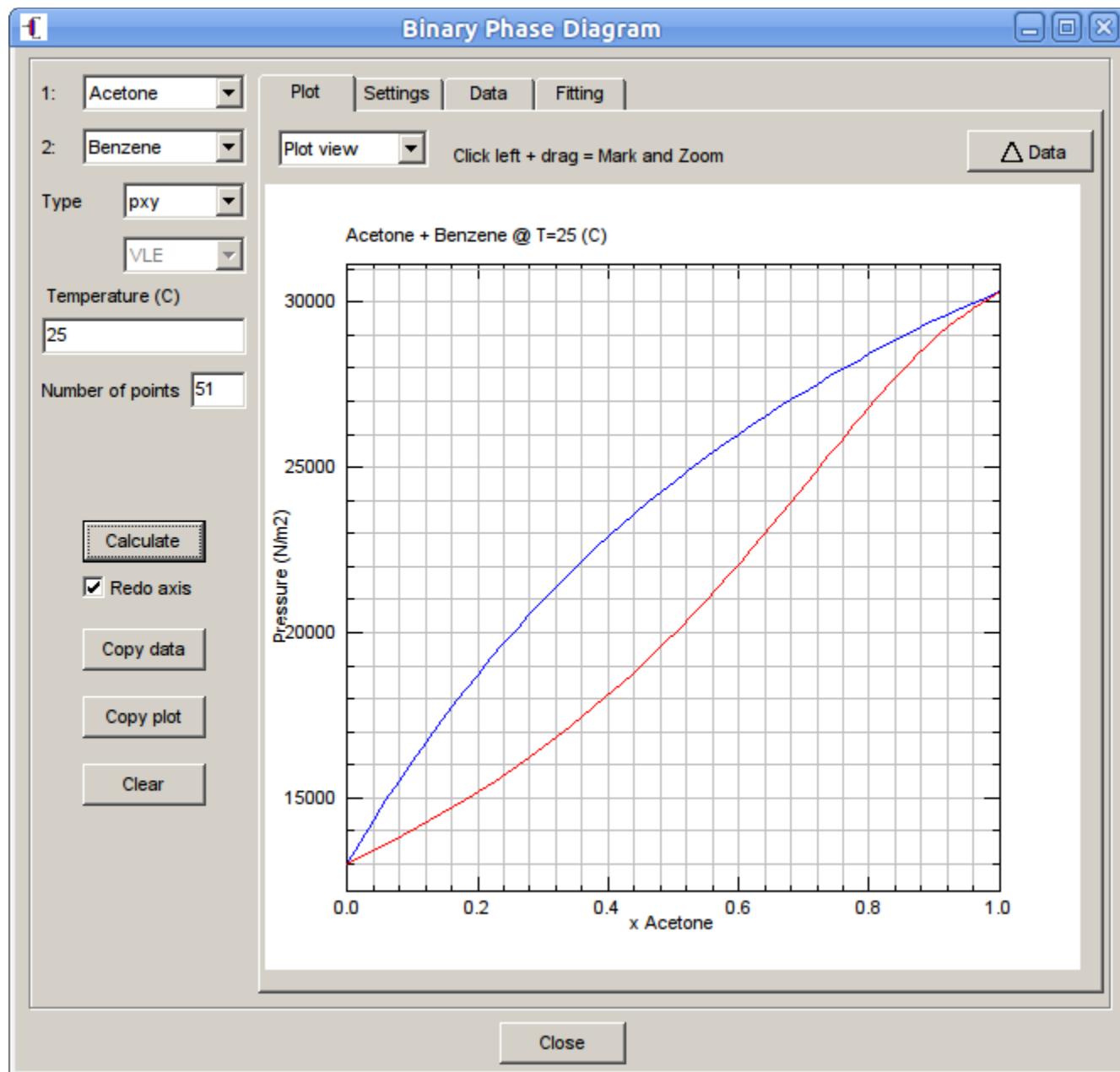
To display our calculations in the same units of measure, select "units" in the navigator. Our experimental data was in degrees Celcius and torr (mm Hg). Since torr is not part of the standard list of pressure units you must type it in the edit box. ChemSep allows you to do so and thus compose all kinds of personal units of measure. ChemSep knows most chemical engineering units and all the prefixes to scale them.



Now save the file under a descriptive name, for example "bvle_acetone_benzene_t25.sep".

VLE model predictions

Then go to Analysis - Phase diagrams - Binary menu option. This opens a window to generate our pxy diagram. Select the type of diagram (pxy) and phase equilibrium (VLE) as well the condition (temperature = 25C) and click on calculate to generate the phase diagram:



VLE Data

Binary VLE data for Acetone and Benzene was published by A. Tasic, B. Djordjevic, D. Grozdanic, N. Afgan, D. Malic, in *Chem. Eng. Sci.* (1978), **33**, pp. 189-197. We created a text file that contains their data as shown below:

```
# file=bvle_acetone_benzene_t25.txt
# ref=ces33p189
# title=P-xy data for acetone (1051) / benzene (501) at 25 C in torr
# fullref=A.Tasic, B.Djordjevic, D.Grozdanic, N.Afgan, D.Malic, Chem.Eng.Sci. (1978), 33, pp. 189-197

pxy@T=25C
95.05  0      0
116.65 0.082  0.248
137.2  0.185  0.416
156.3  0.307  0.55
169.3  0.401  0.632
182.1  0.505  0.703
191.2  0.59   0.755
203.2  0.704  0.824
213.4  0.8055 0.882
220.95 0.8955  0.936
222.35 0.909   0.944
225.05 0.932   0.958
230.4  1      1
```

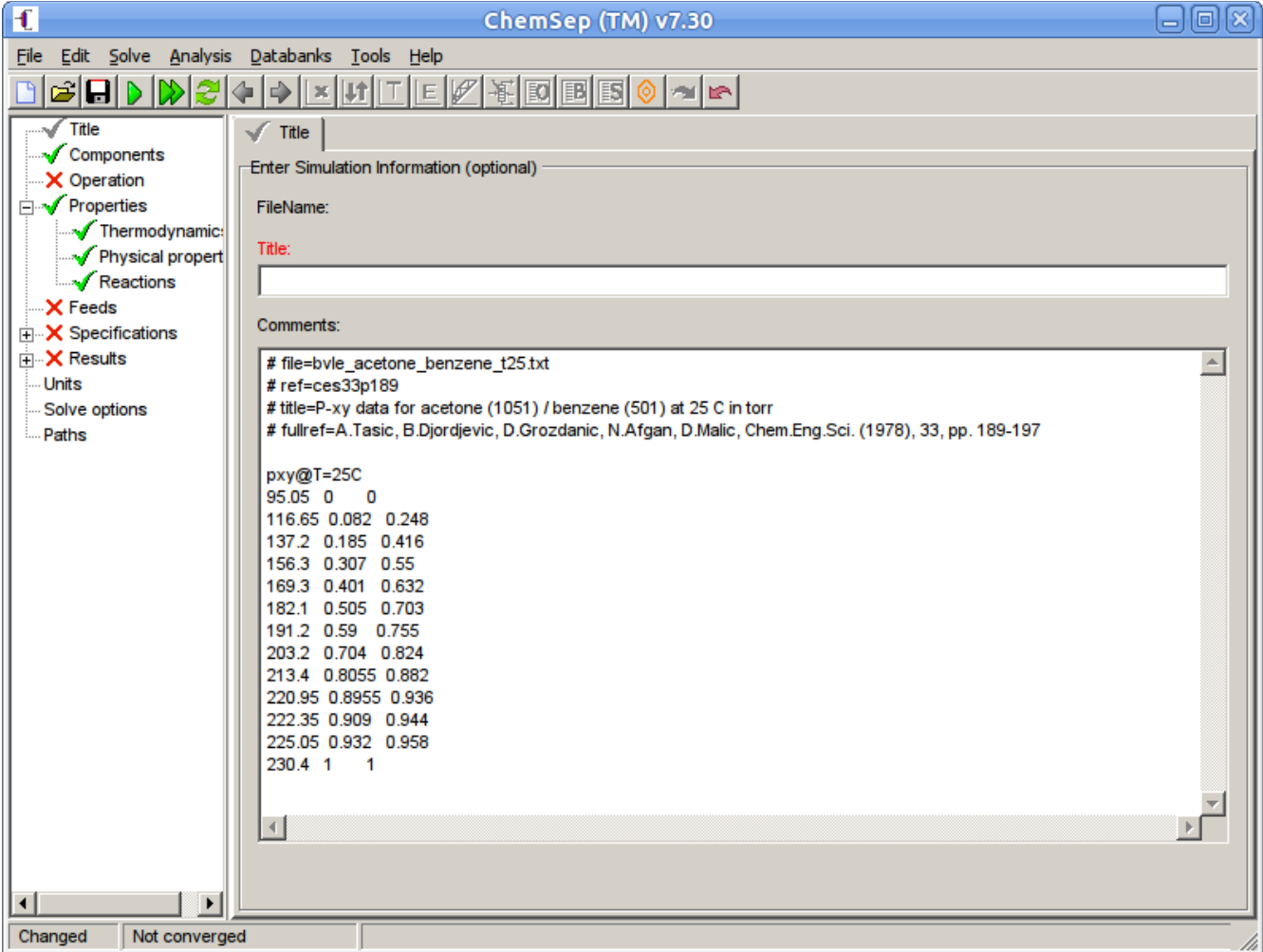
Since acetone boils at a lower temperature than benzene it comes first. As a last part of the file we add a comment line that specifies the conditions at which the measurements were taken; here at constant temperature of 25 C and the units for pressure.

It is important to note that pressure must be identified by a lower-case p.

Note that the numerical values in the table are separated by tabs. ChemSep's import option for binary VLE data also allows spaces, comma's, or semicolons as separators. It is important that you include a line describing the type of data in each column. With the "Copy data" button you can copy the data to the clipboard and from there to a sep file or a text file. Be sure to always include the complete reference to the original article and a descriptive title. Use specific set of journal abbreviations and refer to the volume and first page of the publication so that will be easy to find the original source at some point in the future; in this case "ces33p189". The title and reference are put on lines that start with a "#" to indicate the line does not contain data. You can have as many lines with "comments as needed as long as each of them starts with the "#". **You MUST have at least one comment line.**

Adding the data to ChemSep

Copy the data file above into the space for **Comments** on the **Title** panel as shown below.



The screenshot shows the ChemSep (TM) v7.30 software interface. The main window is titled "ChemSep (TM) v7.30" and has a menu bar with "File", "Edit", "Solve", "Analysis", "Databanks", "Tools", and "Help". Below the menu bar is a toolbar with various icons. On the left side, there is a tree view showing the simulation setup:

- ✓ Title
- ✓ Components
- ✗ Operation
- [-] Properties
 - ✓ Thermodynamic
 - ✓ Physical propert
 - ✓ Reactions
- ✗ Feeds
- [-] Specifications
- ✗ Results
- [-] Units
- [-] Solve options
- [-] Paths

The main panel is titled "Title" and contains the following fields:

- Enter Simulation Information (optional)
- FileName:
- Title:
- Comments:

The Comments field contains the following text:

```
# file=bvle_acetone_benzene_t25.txt
# ref=ces33p189
# title=P-xy data for acetone (1051) / benzene (501) at 25 C in torr
# fullref=A.Tasic, B.Djordjevic, D.Grozdanic, N.Afgan, D.Malic, Chem.Eng.Sci. (1978), 33, pp. 189-197

pxy@T=25C
95.05 0 0
116.65 0.082 0.248
137.2 0.185 0.416
156.3 0.307 0.55
169.3 0.401 0.632
182.1 0.505 0.703
191.2 0.59 0.755
203.2 0.704 0.824
213.4 0.8055 0.882
220.95 0.8955 0.936
222.35 0.909 0.944
225.05 0.932 0.958
230.4 1 1
```

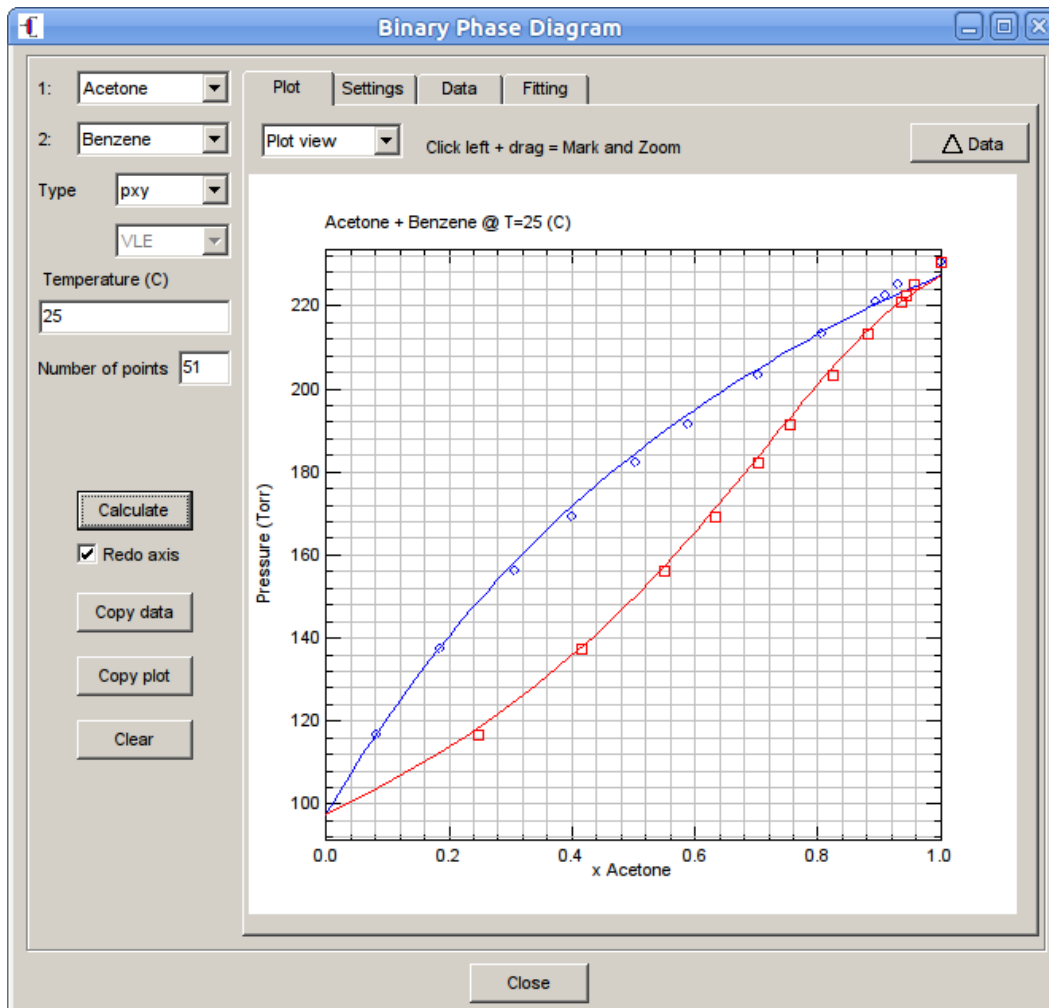
At the bottom of the window, there are two status indicators: "Changed" and "Not converged".

Comparing experimental data with the selected model predictions

Now we want to make a comparison of the model predictions with the experimental data. For this we must load the data either from a file or from the comments section. For both methods you must click the "file open" icon next to data. In our case we must click **Yes** when asked to **Load data from comments field**. This loads the information from the comments page onto the data line (all in one line) – as shown below:

```
pxy;  
T=25C, p=95.05, x=0, y=0;  
T=25C, p=116.65, x=0.082, y=0.248;  
T=25C, p=137.2, x=0.185, y=0.416;  
T=25C, p=156.3, x=0.307, y=0.55;  
T=25C, p=169.3, x=0.401, y=0.632;  
T=25C, p=182.1, x=0.505, y=0.703;  
T=25C, p=191.2, x=0.59, y=0.755;  
T=25C, p=203.2, x=0.704, y=0.824;  
T=25C, p=213.4, x=0.8055, y=0.882;  
T=25C, p=220.95, x=0.8955, y=0.936;  
T=25C, p=222.35, x=0.909, y=0.944;  
T=25C, p=225.05, x=0.932, y=0.958;  
T=25C, p=230.4, x=1, y=1;
```

We see the data is processed: the pxy identifier is repeated and then used for identifying each data item, separated by comma's. The data points themselves are separated by semicolons. Note that the original data did not have units, so no conversions are done. The diagram now has the points shown as entered:



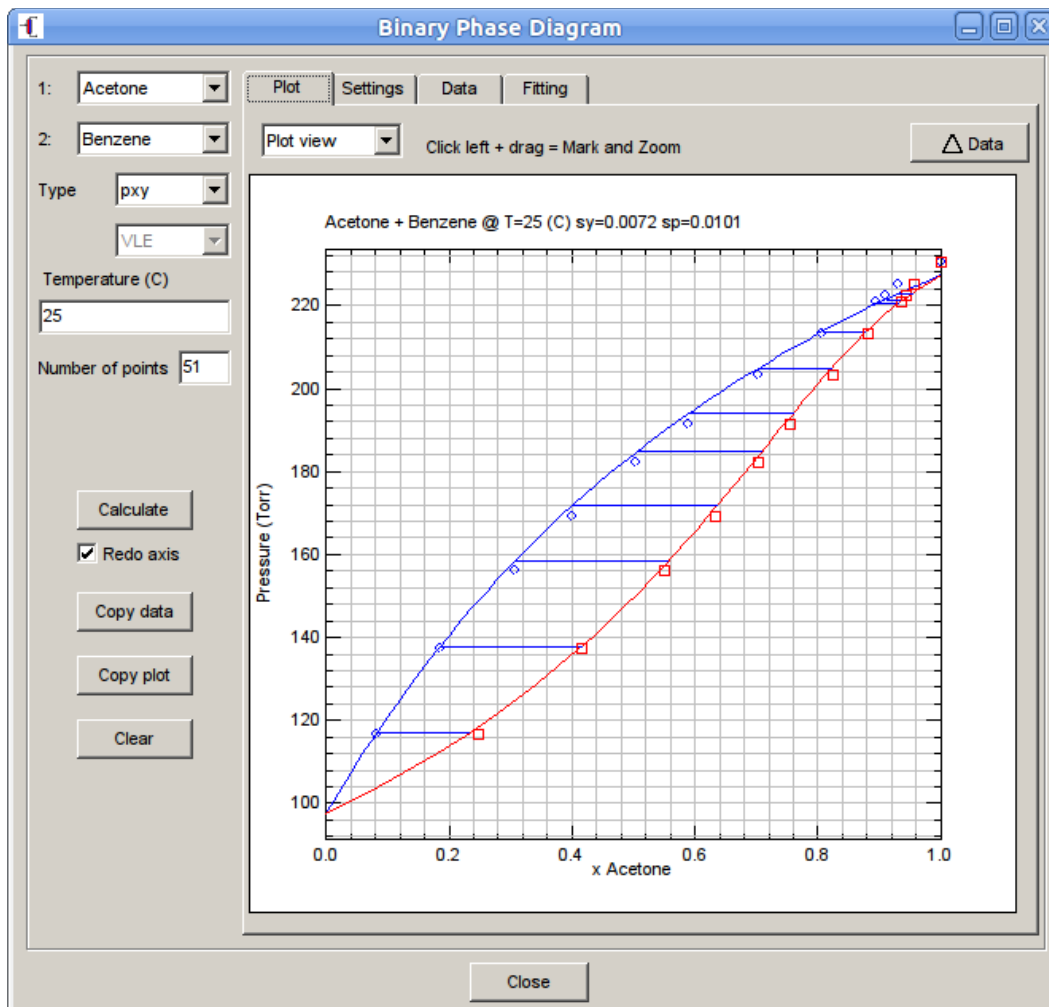
Calculating standard deviations in y and p

To quantify the deviations between the model and the experimental points we can compute the standard deviations by clicking the " Δ Data" button. This computes for each point the pressure p and vapor fraction z that is in equilibrium with the measured liquid composition x and the specified temperature 25°C. ChemSep adds these to the the data line:

pxy;
T=25C, p=95.05, x=0, y=0;
T=25C, p=116.65, x=0.082, y=0.248, q=116.8838, z=0.231121;
T=25C, p=137.2, x=0.185, y=0.416, q=137.7182, z=0.41474;
T=25C, p=156.3, x=0.307, y=0.55, q=158.3699, z=0.556888;
T=25C, p=169.3, x=0.401, y=0.632, q=171.8375, z=0.636968;
T=25C, p=182.1, x=0.505, y=0.703, q=184.715, z=0.70868;
T=25C, p=191.2, x=0.59, y=0.755, q=193.9634, z=0.75956;
T=25C, p=203.2, x=0.704, y=0.824, q=204.9288, z=0.822477;
T=25C, p=213.4, x=0.8055, y=0.882, q=213.5504, z=0.877825;
T=25C, p=220.95, x=0.8955, y=0.936, q=220.388, z=0.930096;
T=25C, p=222.35, x=0.909, y=0.944, q=221.3438, z=0.938449;
T=25C, p=225.05, x=0.932, y=0.958, q=222.9299, z=0.953063;
T=25C, p=230.4, x=1, y=1;

It also computes the relative standard deviations (only for the binary points) and adds them to the title of the diagram: sy is the standard deviation in the vapor composition and sp is the standard deviation in pressure.

In this case most of the deviation in the pxy diagram is caused by the Antoine model not being good enough in this case at predicting the pure component vapor pressures.



Selecting the UNIQUAC activity coefficient model and interaction parameters

We now return to the thermodynamic model selections and select the UNIQUAC model and load the parameters from the library:

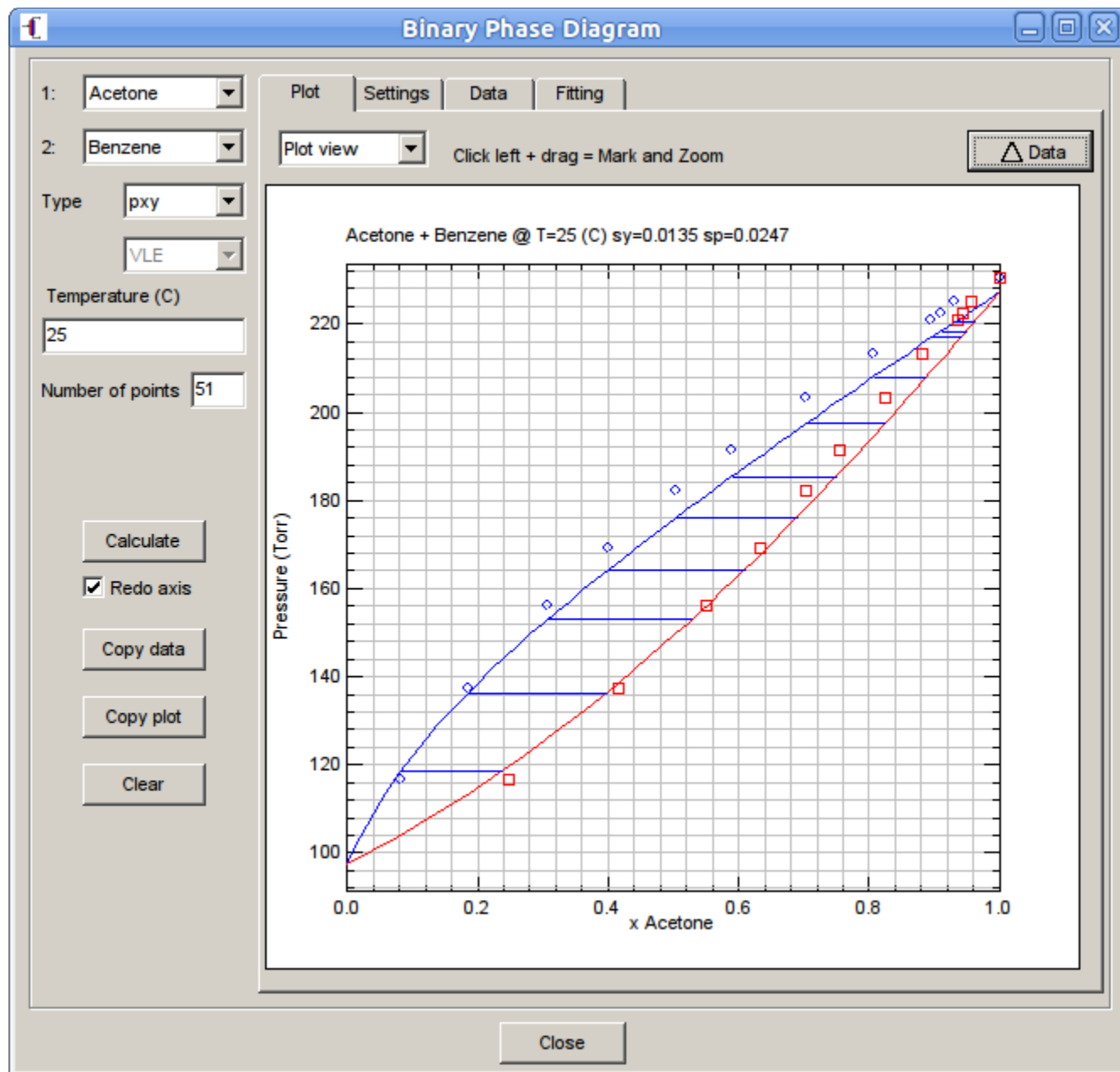
The screenshot shows the ChemSep (TM) v7.30 software interface. The main window is titled "ChemSep (TM) v7.30" and has a menu bar with "File", "Edit", "Solve", "Analysis", "Databanks", "Tools", and "Help". Below the menu bar is a toolbar with various icons. On the left side, there is a tree view with the following items: Title (checked), Components (checked), Operation (unchecked), Properties (checked), Thermodynamic (checked), Physical property (checked), Reactions (checked), Feeds (unchecked), Specifications (unchecked), Results (unchecked), Units (checked), Solve options (checked), and Paths (checked). The main area is divided into several sections. At the top, there are three tabs: "Thermodynamics" (checked), "Physical properties" (checked), and "Reactions" (checked). Below these tabs is the "Select Thermodynamic Models" section, which contains several dropdown menus: "K-value" (DECHEMA), "Equation of state" (Ideal gas law), "Activity coefficient" (UNIQUAC), "Vapour pressure" (Antoine), and "Enthalpy" (Excess). To the right of these is the "Enthalpy / Exergy" section, which includes "Reference state" (Vapour, 25.00 (C)), "Heat of formation" (Excluded), "Surroundings T" (25.0000 (C)), "Heat Capacity IG" (T correlation), and "Heat Capacity L" (Molar average). There is also a checkbox for "Henry's law components". Below this is the "Enter Thermodynamic Model Parameters (when required)" section, which is currently set to "UNIQUAC". It includes "Units" (J/mol), a checkbox for "BIP estimation", "BIP T est. (C)" (76.8500), and "T dependence" (None). There are "Reset", "Load", and "Save" buttons. Below the buttons is a table with the following data:

i - j	A-ij	A-ji
Acetone - Benzene	-1501.73	2528.31

At the bottom of the window, there are two status indicators: "Changed" and "Not converged".

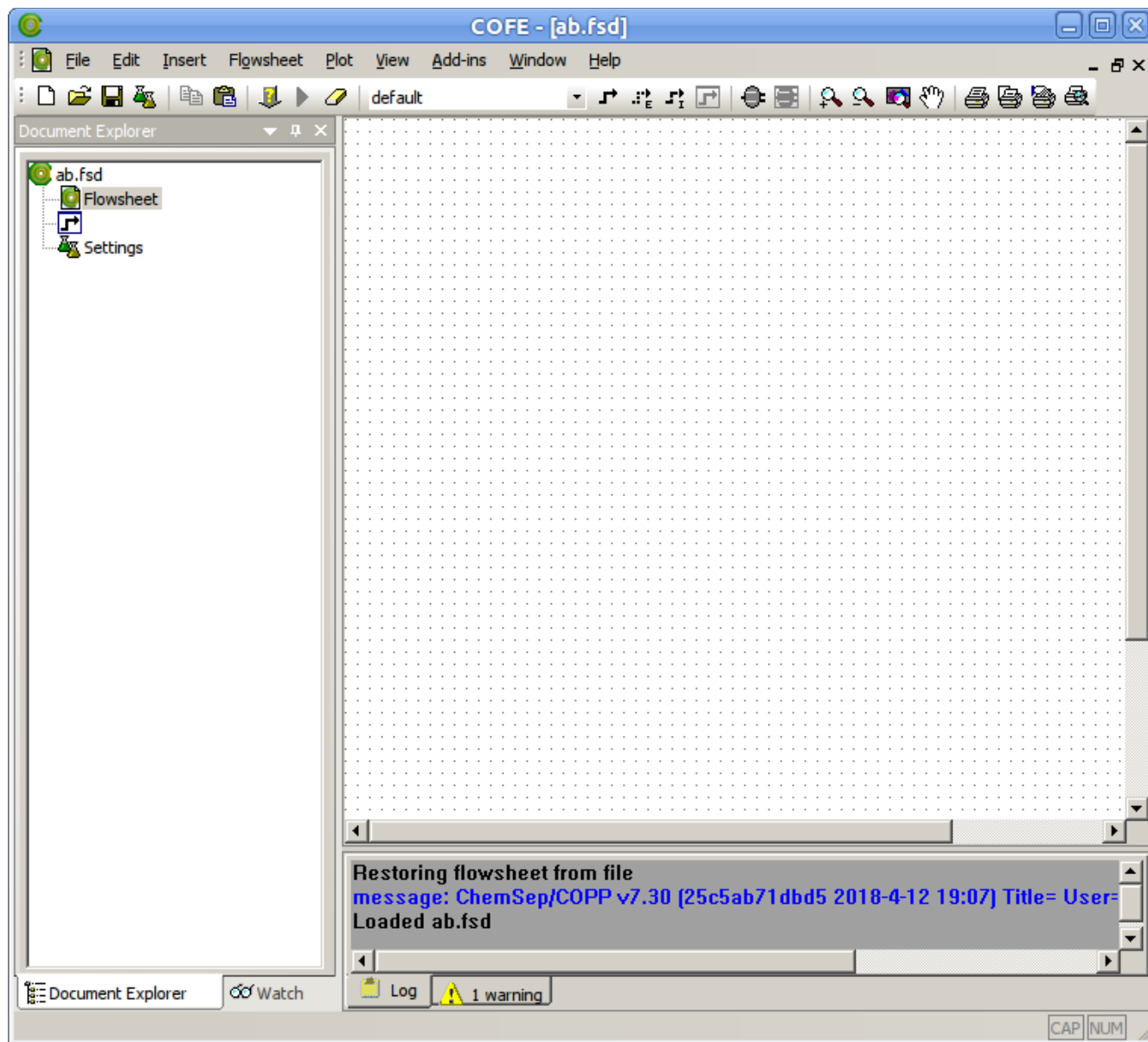
UNIQUAC fit of the VLE data

When we return to the phase diagrams panel and redraw the diagram we will obtain a fit that is less good - deviations in pressure increase by more than a factor two - but the curvature of the dew and bubble point lines is correct:



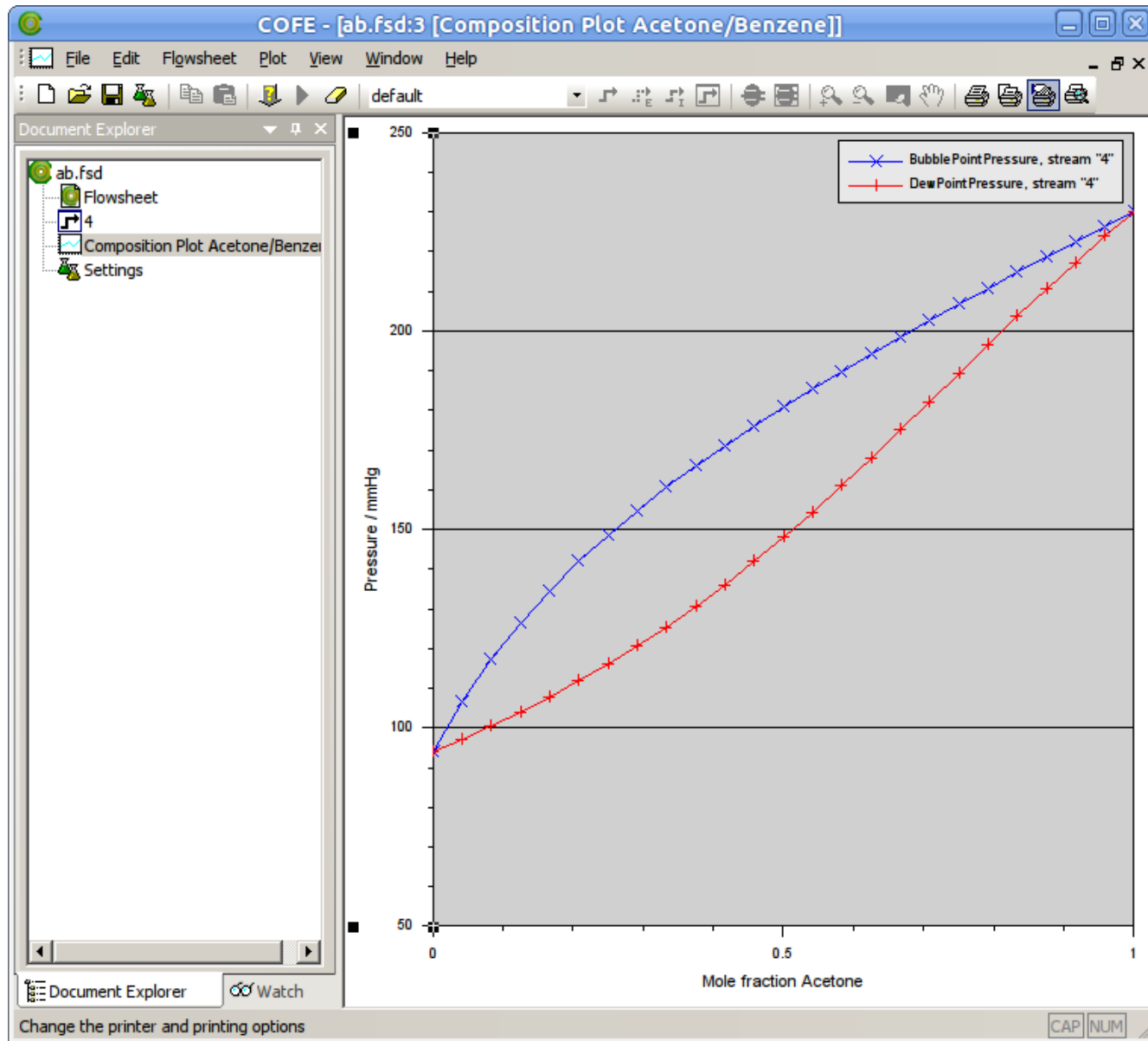
Thus, lower relative deviations of pressure and mole fractions aren't necessarily indicative for a qualitative better description of the binary VLE. This is due to the errors in the pure component vapour pressures. Errors over half of the concentration range are introduced when a pure component bubble point temperature is off by just one or two degrees! We leave it to the reader as an exercise to select different models for the vapor pressure to see how the predictions can vary.

Now switch back to the UNIFAC model and export the file to a COCO flowsheet by using the “Export to flowsheet” option in the File menu. Of course this only works if you have installed the COCO flowsheet program (which you can download from www.cocosimulator.org). After you specified a file name e.g. ab.fsd to save under the COCO program opens with the newly defined ChemSep CAPE-OPEN defined thermodynamic Property Package (ChemSep/COPP):



The message in blue shows that the property package is loaded and initialized.

To be able to generate a pxy plot in COCO you first need to add a stream onto the flowsheet with the Stream option of the Insert menu and clicking an begin and end point on the process flow diagram area (i.e. the dotted area). Double click the stream to get the stream editor and enter 298.15 K for the Temperature. Then you can use the PXY option of the Plot menu to generate a pxy diagram of the specified stream. You will get a similar looking pxy diagram as before. but with Pascal as units on the Pressure axis. Double click the pressure axis title and you can modify the units to Torr by clicking on the [Change] button on the "Scale" panel. The result then looks like:



The power of ChemSep is that you can use it as property package in any CAPE-OPEN simulation environment such as ASPEN PLUS, COCO, Pro/II, gProms, ProSim, UNISIM Design, etc.